

AP20 Rec'd PCT/PTO 05 MAY 2006

2-Halo-6-alkylphenyl-substituted spirocyclic tetramic acid derivatives

The invention relates to novel 2-halo-6-alkylphenyl-substituted spirocyclic tetramic acid derivatives, to a plurality of processes and intermediates for their preparation and to their use as pesticides and/or herbicides. Moreover, the invention relates to novel selective herbicidal active compound combinations comprising both the 2-halo-6-alkylphenyl-substituted spirocyclic tetramic acid derivatives and at least one crop plant compatibility-improving compound, which combinations can be used with particularly good results for the selective control of weeds in various crops of useful plants.

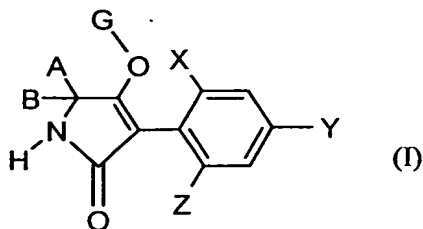
3-Acylpyrrolidine-2,4-diones are described as having pharmaceutical properties (S. Suzuki et al. Chem. Pharm. Bull. 15 1120 (1967)). Furthermore, N-phenylpyrrolidine-2,4-diones were synthesized by R. Schmierer and H. Mildenberger (Liebigs Ann. Chem. 1985, 1095). A biological activity of these compounds has not been described.

EP-A-0 262 399 and GB-A-2 266 888 disclose compounds of a similar structure (3-arylpyrrolidine-2,4-diones); however, a herbicidal, insecticidal or acaricidal action of these compounds has hitherto not been described. Unsubstituted bicyclic 3-arylpyrrolidine-2,4-dione derivatives (EP-A-355 599 and EP-A-415 211) and substituted monocyclic 3-arylpyrrolidine-2,4-dione derivatives (EP-A-377 893 and EP-A-442 077) having herbicidal, insecticidal or acaricidal action are known.

Also known are polycyclic 3-arylpyrrolidine-2,4-dione derivatives (EP-A-442 073) and 1H-arylpyrrolidinedione derivatives (EP-A-456 063, EP-A-521 334, EP-A-596 298, EP-A-613 884, EP-A-613 885, WO 94/01 997, WO 95/26954, WO 95/20 572, EP-A 0 668 267, WO 96/25 395, WO 96 35 664, WO 97/01 535, WO 97/02 243, WO 97/36 868, WO 97/43275, WO/98/05638, WO 98/06721, WO 98/25928, WO 99/16748, WO 99/24437, WO 99/43649, WO 99/48869, WO 99/55673, WO 01/09092, WO 01/17972, WO 01/23354, WO 01/74770 and WO 03/013249).

However, in particular at low application rates and concentrations, the activity and the activity spectrum of these compounds are not always entirely satisfactory. Moreover, the compatibility with plants of these compounds is not always sufficient.

This invention now provides novel compounds of the formula (I)



in which

X represents halogen,

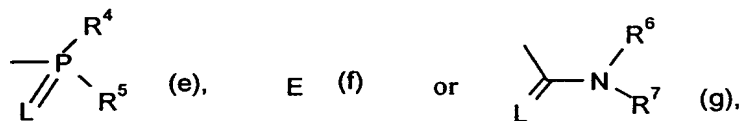
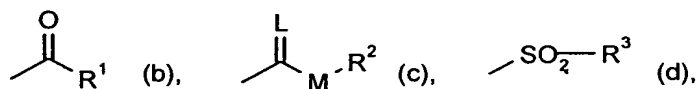
Y represents alkyl and

5 Z represents C_2-C_6 -alkyl,

A and B together with the carbon atom to which they are attached represent a saturated or unsaturated C_3-C_8 -ring which optionally contains at least one heteroatom and which is optionally substituted by alkoxy or haloalkyl,

and

10 G represents hydrogen (a) or represents one of the groups



in which

E represents a metal ion equivalent or an ammonium ion,

L represents oxygen or sulphur,

15 M represents oxygen or sulphur,

R^1 represents in each case optionally substituted alkyl, alkenyl, alkoxyalkyl, alkylthioalkyl or polyalkoxyalkyl or represents in each case optionally halogen-, alkyl- or alkoxy-substituted

cycloalkyl or heterocyclyl or represents in each case optionally substituted phenyl, phenylalkyl, phenylalkenyl or hetaryl,

5 R^2 represents in each case optionally halogen-substituted alkyl, alkenyl, alkoxyalkyl or polyalkoxyalkyl or represents in each case optionally substituted cycloalkyl, phenyl or benzyl,

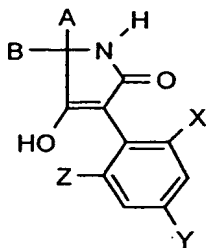
R^3 , R^4 and R^5 independently of one another represent in each case optionally halogen-substituted alkyl, alkoxy, alkylamino, dialkylamino, alkylthio, alkenylthio or cycloalkylthio or represent in each case optionally substituted phenyl, benzyl, phenoxy or phenylthio,

10 R^6 and R^7 independently of one another represent hydrogen, represent in each case optionally halogen-substituted alkyl, cycloalkyl, alkenyl, alkoxy, alkoxyalkyl, represent in each case optionally substituted phenyl or benzyl, or together with the N atom to which they are attached form an optionally substituted cycle which optionally contains oxygen or sulphur.

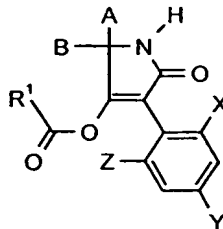
Depending inter alia on the nature of the substituents, the compounds of the formula (I) can be present as geometrical and/or optical isomers or isomer mixtures of varying composition which, if
15 appropriate, can be separated in a customary manner. The present invention provides both the pure isomers and the isomer mixtures, their preparation and use and compositions comprising them. However, hereinbelow, for the sake of simplicity, only compounds of the formula (I) are referred to, although what is meant are both the pure compounds and, if appropriate, also mixtures having varying proportions of isomeric compounds.

20 Taking into account the different meanings (a), (b), (c), (d), (e), (f) and (g) of group G, the following principle structures (I-a) to (I-g) result:

(I-a):

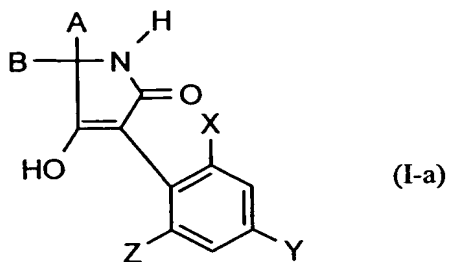


(I-b):



A, B, E, L, M, X, Y, Z, R^1 , R^2 , R^3 , R^4 , R^5 , R^6 and R^7 are as defined above.

5 (A) Compounds of the formula (I-a),

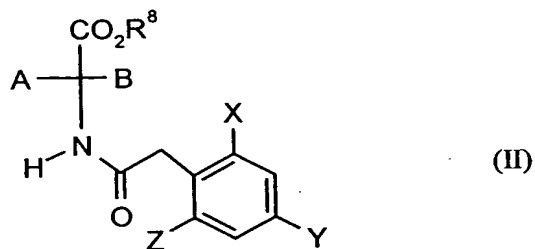


in which

A, B, X, Y and Z are as defined above,

are obtained when

5 compounds of the formula (II),



in which

A, B, X, Y and Z are as defined above,

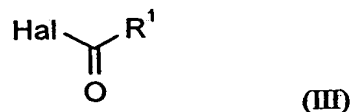
and

10 R^8 represents alkyl (preferably C_1 - C_6 -alkyl),

are condensed intramolecularly in the presence of a diluent and in the presence of a base.

(B) Compounds of the formula (I-b) shown above in which A, B, R^1 , X, Y and Z are as defined above are obtained when compounds of the formula (I-a) shown above in which A, B, X, Y and Z are as defined above are reacted

15 α) with acid halides of the formula (III),



in which

R^1 is as defined above and

Hal represents halogen (in particular chlorine or bromine)

or

- 5 β) with carboxylic anhydrides of the formula (IV),



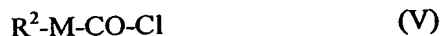
in which

R^1 is as defined above,

if appropriate in the presence of a diluent and if appropriate in the presence of an acid binder.

- 10 (C) Compounds of the formula (I-c) shown above in which A, B, R^2 , M, X, Y and Z are as defined above and L represents oxygen are obtained when compounds of the formula (I-a) shown above in which A, B, X, Y and Z are as defined above are in each case reacted

with chloroformic esters or with chloroformic thioesters of the formula (V),



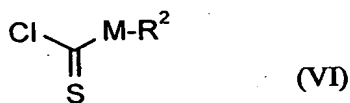
- 15 in which

R^2 and M are as defined above,

if appropriate in the presence of a diluent and if appropriate in the presence of an acid binder.

- (D) Compounds of the formula (I-c) shown above in which A, B, R^2 , M, X, Y and Z are as defined above and L represents sulphur are obtained when compounds of the formula (I-a) shown above in which A, B, X, Y and Z are as defined above are in each case reacted
- 20

- α) with chloromonothioformic esters or chlorodithioformic esters of the formula (VI),



in which

M and R² are as defined above,

if appropriate in the presence of a diluent and if appropriate in the presence of an acid binder

or

β) with carbon disulphide and subsequently with compounds of the formula (VII),



in which

R² is as defined above and

Hal represents chlorine, bromine or iodine,

if appropriate in the presence of a diluent and if appropriate in the presence of a base.

10 (E) Compounds of the formula (I-d) shown above in which A, B, R³, X, Y and Z are as defined above are obtained when compounds of the formula (I-a) shown above in which A, B, X, Y and Z are as defined above are in each case reacted

with sulphonyl chlorides of the formula (VIII),



15 in which

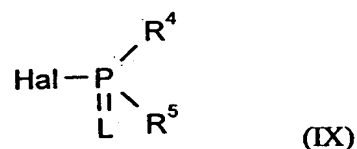
R³ is as defined above,

if appropriate in the presence of a diluent and if appropriate in the presence of an acid binder.

(F) Compounds of the formula (I-e) shown above in which A, B, L, R⁴, R⁵, X, Y and Z are as defined above are obtained when compounds of the formula (I-a) shown above in which A, B, X, Y and Z are as defined above are in each case reacted

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with phosphorus compounds of the formula (IX),



in which

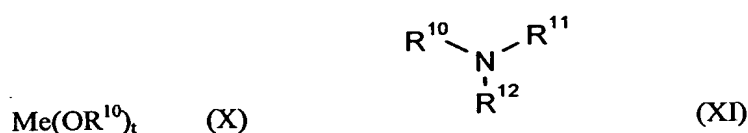
L, R⁴ and R⁵ are as defined above and

Hal represents halogen (in particular chlorine or bromine),

if appropriate in the presence of a diluent and if appropriate in the presence of an acid binder.

- 5 (G) Compounds of the formula (I-f) shown above in which A, B, E, X, Y and Z are as defined above are obtained when compounds of the formula (I-a) in which A, B, X, Y and Z are as defined above are in each case reacted

with metal compounds or amines of the formulae (X) and (XI), respectively,



in which

- 10 Me represents a mono- or divalent metal (preferably an alkali metal or alkaline earth metal, such as lithium, sodium, potassium, magnesium or calcium),

t represents the number 1 or 2 and

R¹⁰, R¹¹, R¹² independently of one another represent hydrogen or alkyl (preferably C₁-C₈-alkyl),

- 15 if appropriate in the presence of a diluent.

- (H) Compounds of the formula (I-g) shown above in which A, B, L, R⁶, R⁷, X, Y and Z are as defined above are obtained when compounds of the formula (I-a) shown above in which A, B, X, Y and Z are as defined above are in each case reacted

α) with isocyanates or isothiocyanates of the formula (XII),

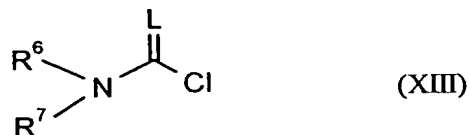


in which

R⁶ and L are as defined above,

if appropriate in the presence of a diluent and if appropriate in the presence of a catalyst, or

- β) with carbamoyl chlorides or thiocarbamoyl chlorides of the formula (XIII),

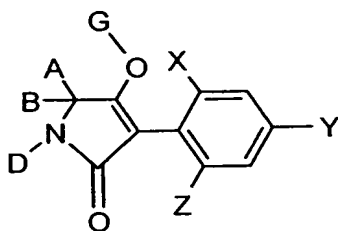


in which

L, R⁶ and R⁷ are as defined above,

if appropriate in the presence of a diluent and if appropriate in the presence of an acid binder.

- 5 In April 2002, in the context of the European examination proceedings of EP-A-835 243, the following tetramic acid derivatives were filed subsequently:



Ex. No. in EP-A 835 243	X	Y	Z	D	A	B	G	m.p.°C
I-1-a-45	Br	CH ₃	C ₂ H ₅	H	-(CH ₂) ₂ -CHCH ₃ - (CH ₂) ₂ -		H	190
I-1-a-46	Br	CH ₃	C ₂ H ₅	H	CH ₃	CH ₃	H	202
I-1-b-73	Br	CH ₃	C ₂ H ₅	H	-(CH ₂) ₂ -CHCH ₃ - (CH ₂) ₂ -		H ₅ C ₂ -O-CH ₂ - CO	165

- 10 Furthermore, it has been found that the novel compounds of the formula (I) are highly active pesticides, preferably insecticides and/or acaricides and/or herbicides.

- 15 Surprisingly, it has now also been found that certain substituted cyclic ketoenols, when used together with the crop plant compatibility-improving compounds (safeners/antidotes) described below, are highly suitable for preventing damage to the crop plants and can be used particularly advantageously as broad-spectrum effective combination preparations for the selective control of unwanted plants in crops of useful plants, such as, for example, in cereals, but also maize, soybeans and rice.

The invention also provides selective herbicidal compositions comprising an effective amount of a combination of active compounds comprising the components

- (a') at least one substituted, cyclic ketoenol of the formula (I) in which A, B, G, X, Y and Z are as defined above

and

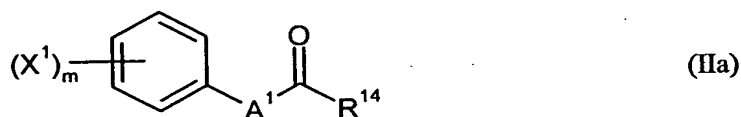
- (b) at least one crop plant compatibility-improving compound from the following group of compounds:

4-dichloroacetyl-1-oxa-4-azaspiro[4.5]decane (AD-67, MON-4660), 1-dichloroacetylhexahydro-3,3,8a-trimethylpyrrolo[1,2-a]pyrimidin-6(2H)-one (dicyclonon, BAS-145138), 4-dichloroacetyl-3,4-dihydro-3-methyl-2H-1,4-benzoxazine (benoxacor), 1-methylhexyl 5-chloroquinoline-8-oxyacetate (cloquintocet-mexyl - cf. also related compounds in EP-A-86750, EP-A-94349, EP-A-191736, EP-A-492366), 3-(2-chlorobenzyl)-1-(1-methyl-1-phenylethyl)urea (cumyluron), α -(cyanomethoximino)phenylacetoneitrile (cyometrinil), 2,4-dichlorophenoxyacetic acid (2,4-D), 4-(2,4-dichlorophenoxy)butyric acid (2,4-DB), 1-(1-methyl-1-phenylethyl)-3-(4-methylphenyl)urea (daimuron, dymron), 3,6-dichloro-2-methoxybenzoic acid (dicamba), S-1-methyl 1-phenylethyl piperidine-1-thiocarboxylate (dimepiperate), 2,2-dichloro-N-(2-oxo-2-(2-propenylamino)ethyl)-N-(2-propenyl)acetamide (DKA-24), 2,2-dichloro-N,N-di-2-propenylacetamide (dichlormid), 4,6-dichloro-2-phenylpyrimidine (fencloirim), ethyl 1-(2,4-dichlorophenyl)-5-trichloromethyl-1H-1,2,4-triazole-3-carboxylate (fenchlorazole-ethyl - cf. also related compounds in EP-A-174562 and EP-A-346620), phenylmethyl 2-chloro-4-trifluoromethylthiazole-5-carboxylate (flurazole), 4-chloro-N-(1,3-dioxolan-2-ylmethoxy)- α -trifluoroacetophenone oxime (fluxofenim), 3-dichloroacetyl-5-(2-furanyl)-2,2-dimethyloxazolidine (furilazole, MON-13900), ethyl 4,5-dihydro-5,5-diphenyl-3-isoxazolecarboxylate (isoxadifen-ethyl - cf. also related compounds in WO-A-95/07897), 1-(ethoxycarbonyl)ethyl 3,6-dichloro-2-methoxybenzoate (lactidichlor), (4-chloro-o-tolyloxy)acetic acid (MCPA), 2-(4-chloro-o-tolyloxy)propionic acid (mecoprop), diethyl 1-(2,4-dichlorophenyl)-4,5-dihydro-5-methyl-1H-pyrazole-3,5-dicarboxylate (mefenpyr-diethyl - cf. also related compounds in WO-A-91/07874), 2-dichloromethyl-2-methyl-1,3-dioxolane (MG-191), 2-propenyl-1-oxa-4-azaspiro[4.5]decane-4-carbodithioate (MG-838), 1,8-naphthalic anhydride, α -(1,3-dioxolan-2-ylmethoximino)phenylacetoneitrile (oxabetrinil), 2,2-dichloro-N-(1,3-dioxolan-2-ylmethyl)-N-(2-propenyl)acetamide (PPG-1292), 3-dichloroacetyl-2,2-dimethyloxazolidine (R-28725), 3-dichloroacetyl-2,2,5-trimethyloxazolidine (R-29148), 4-(4-chloro-o-tolyl)butyric acid, 4-(4-chlorophenoxy)butyric acid, diphenylmethoxyacetic acid, methyl diphenylmethoxyacetate, ethyl diphenylmethoxyacetate, methyl 1-(2-chlorophenyl)-5-phenyl-1H-pyrazole-3-carboxylate, ethyl 1-(2,4-dichlorophenyl)-5-methyl-1H-pyrazole-3-carboxylate, ethyl 1-(2,4-dichlorophenyl)-5-isopropyl-1H-pyrazole-3-carboxylate, ethyl 1-(2,4-dichlorophenyl)-5-(1,1-dimethylethyl)-1H-pyrazole-3-carboxylate, ethyl 1-(2,4-dichlorophenyl)-5-phenyl-

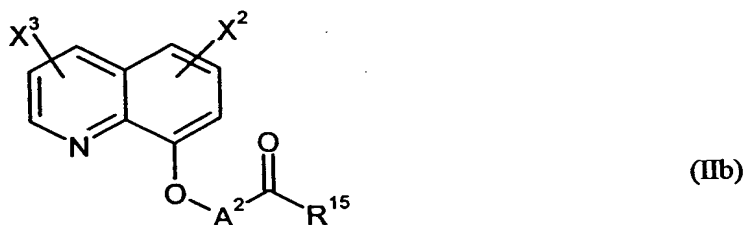
- 1H-pyrazole-3-carboxylate (cf. also related compounds in EP-A-269806 and EP-A-333131), ethyl 5-(2,4-dichlorobenzyl)-2-isoxazoline-3-carboxylate, ethyl 5-phenyl-2-isoxazoline-3-carboxylate, ethyl 5-(4-fluorophenyl)-5-phenyl-2-isoxazoline-3-carboxylate (cf. also related compounds in WO-A-91/08202), 1,3-dimethylbut-1-yl 5-chloroquinoline-8-oxyacetate, 4-allyloxybutyl 5-chloroquinoline-8-oxyacetate, 1-allyloxyprop-2-yl 5-chloroquinoline-8-oxyacetate, methyl 5-chloroquinoxaline-8-oxyacetate, ethyl 5-chloroquinoline-8-oxyacetate, allyl 5-chloroquinoxaline-8-oxyacetate, 2-oxoprop-1-yl 5-chloroquinoline-8-oxyacetate, diethyl 5-chloroquinoline-8-oxy-
 5 malonate, diallyl 5-chloroquinoxaline-8-oxymalonate, diethyl 5-chloroquinoline-8-oxymalonate (cf. also related compounds in EP-A-582198), 4-carboxychroman-4-ylacetic acid (AC-304415, cf.
 10 EP-A-613618), 4-chlorophenoxyacetic acid, 3,3'-dimethyl-4-methoxybenzophenone, 1-bromo-4-chloromethylsulphonylbenzene, 1-[4-(N-2-methoxybenzoylsulphamoyl)phenyl]-3-methylurea (also known as N-(2-methoxybenzoyl)-4-[(methylaminocarbonyl)amino]benzenesulphonamide), 1-[4-(N-2-methoxybenzoylsulphamoyl)phenyl]-3,3-dimethylurea, 1-[4-(N-4,5-dimethylbenzoyl-
 15 sulphonyl)phenyl]-3-methylurea, 1-[4-(N-naphthylsulphamoyl)phenyl]-3,3-dimethylurea, N-(2-methoxy-5-methylbenzoyl)-4-(cyclopropylaminocarbonyl)benzenesulphonamide,

and/or one of the following compounds, defined by general formulae,

of the general formula (IIa)



or of the general formula (IIb)



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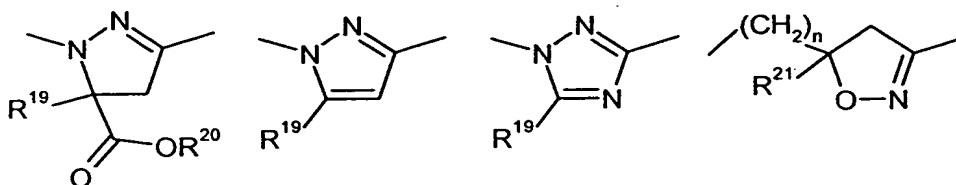
or of the formula (IIc)



where

m represents the number 0, 1, 2, 3, 4 or 5,

A¹ represents one of the divalent heterocyclic groupings shown below,



5 n represents the number 0, 1, 2, 3, 4 or 5,

A² represents optionally C₁-C₄-alkyl- and/or C₁-C₄-alkoxy-carbonyl- and or C₁-C₄-alkenyloxy-carbonyl-substituted alkanediyl having 1 or 2 carbon atoms,

R¹⁴ represents hydroxyl, mercapto, amino, C₁-C₆-alkoxy, C₁-C₆-alkylthio, C₁-C₆-alkylamino or di-(C₁-C₄-alkyl)amino,

10 R¹⁵ represents hydroxyl, mercapto, amino, C₁-C₇-alkoxy, C₁-C₆-alkylthio, C₁-C₆-alkenyloxy, C₁-C₆-alkenyloxy-C₁-C₆-alkoxy, C₁-C₆-alkylamino or di-(C₁-C₄-alkyl)amino,

R¹⁶ represents in each case optionally fluorine-, chlorine- and/or bromine-substituted C₁-C₄-alkyl,

15 R¹⁷ represents hydrogen, in each case optionally fluorine-, chlorine- and/or bromine-substituted C₁-C₆-alkyl, C₂-C₆-alkenyl or C₂-C₆-alkynyl, C₁-C₄-alkoxy-C₁-C₄-alkyl, dioxolanyl-C₁-C₄-alkyl, furyl, furyl-C₁-C₄-alkyl, thienyl, thiazolyl, piperidiny, or optionally fluorine-, chlorine- and/or bromine- or C₁-C₄-alkyl-substituted phenyl,

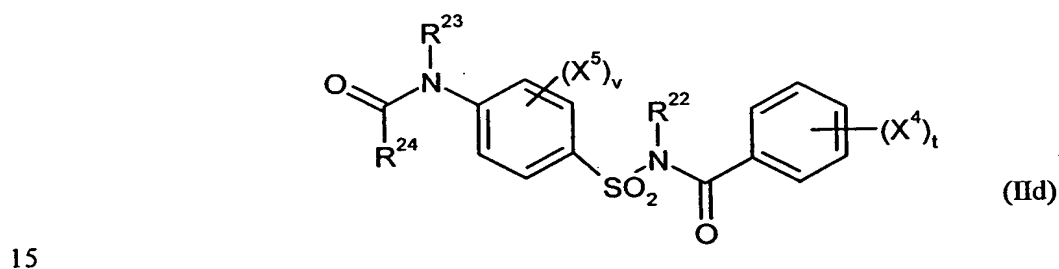
20 R¹⁸ represents hydrogen, in each case optionally fluorine-, chlorine- and/or bromine-substituted C₁-C₆-alkyl, C₂-C₆-alkenyl or C₂-C₆-alkynyl, C₁-C₄-alkoxy-C₁-C₄-alkyl, dioxolanyl-C₁-C₄-alkyl, furyl, furyl-C₁-C₄-alkyl, thienyl, thiazolyl, piperidiny, or optionally fluorine-, chlorine- and/or bromine- or C₁-C₄-alkyl-substituted phenyl,

R¹⁷ and R¹⁸ also together optionally represent C₃-C₆-alkanediyl or C₂-C₅-oxaalkanediyl, each of which is optionally substituted by C₁-C₄-alkyl, phenyl, furyl, a fused benzene ring or by two substituents which, together with the C atom to which they are attached, form a 5- or 6-membered carbocycle,

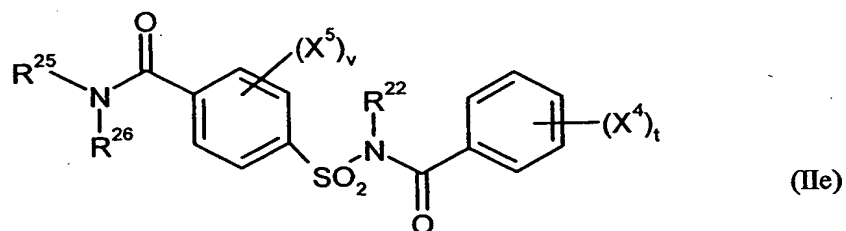
- R^{19} represents hydrogen, cyano, halogen, or represents in each case optionally fluorine-, chlorine- and/or bromine-substituted C_1 - C_4 -alkyl, C_3 - C_6 -cycloalkyl or phenyl,
- R^{20} represents hydrogen, optionally hydroxyl-, cyano-, halogen- or C_1 - C_4 -alkoxy-substituted C_1 - C_6 -alkyl, C_3 - C_6 -cycloalkyl or tri- $(C_1$ - C_4 -alkyl)silyl,
- 5 R^{21} represents hydrogen, cyano, halogen, or represents in each case optionally fluorine-, chlorine- and/or bromine-substituted C_1 - C_4 -alkyl, C_3 - C_6 -cycloalkyl or phenyl,
- X^1 represents nitro, cyano, halogen, C_1 - C_4 -alkyl, C_1 - C_4 -haloalkyl, C_1 - C_4 -alkoxy or C_1 - C_4 -haloalkoxy,
- X^2 represents hydrogen, cyano, nitro, halogen, C_1 - C_4 -alkyl, C_1 - C_4 -haloalkyl, C_1 - C_4 -alkoxy or C_1 -
10 C_4 -haloalkoxy,
- X^3 represents hydrogen, cyano, nitro, halogen, C_1 - C_4 -alkyl, C_1 - C_4 -haloalkyl, C_1 - C_4 -alkoxy or C_1 - C_4 -haloalkoxy,

and/or the following compounds, defined by general formulae,

of the general formula (II_d)



or of the general formula (II_e)



where

t represents the number 0, 1, 2, 3, 4 or 5,

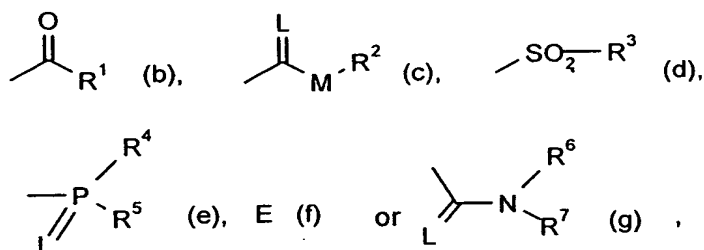
- v represents the number 0, 1, 2, 3, 4 or 5,
- R²² represents hydrogen or C₁-C₄-alkyl,
- R²³ represents hydrogen or C₁-C₄-alkyl,
- 5 R²⁴ represents hydrogen, in each case optionally cyano-, halogen- or C₁-C₄-alkoxy-substituted C₁-C₆-alkyl, C₁-C₆-alkoxy, C₁-C₆-alkylthio, C₁-C₆-alkylamino or di-(C₁-C₄-alkyl)amino, or in each case optionally cyano-, halogen- or C₁-C₄-alkyl-substituted C₃-C₆-cycloalkyl, C₃-C₆-cycloalkyloxy, C₃-C₆-cycloalkylthio or C₃-C₆-cycloalkylamino,
- 10 R²⁵ represents hydrogen, optionally cyano-, hydroxyl-, halogen- or C₁-C₄-alkoxy-substituted C₁-C₆-alkyl, in each case optionally cyano- or halogen-substituted C₃-C₆-alkenyl or C₃-C₆-alkynyl, or optionally cyano-, halogen- or C₁-C₄-alkyl-substituted C₃-C₆-cycloalkyl,
- 15 R²⁶ represents hydrogen, optionally cyano-, hydroxyl-, halogen- or C₁-C₄-alkoxy-substituted C₁-C₆-alkyl, in each case optionally cyano- or halogen-substituted C₃-C₆-alkenyl or C₃-C₆-alkynyl, optionally cyano-, halogen- or C₁-C₄-alkyl-substituted C₃-C₆-cycloalkyl, or optionally nitro-, cyano-, halogen-, C₁-C₄-alkyl-, C₁-C₄-haloalkyl, C₁-C₄-alkoxy- or C₁-C₄-haloalkoxy-substituted phenyl, or together with R²⁵ represents in each case optionally C₁-C₄-alkyl-substituted C₂-C₆-alkanediyl or C₂-C₅-oxaalkanediyl,
- X⁴ represents nitro, cyano, carboxyl, carbamoyl, formyl, sulphamoyl, hydroxyl, amino, halogen, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy or C₁-C₄-haloalkoxy, and
- 20 X⁵ represents nitro, cyano, carboxyl, carbamoyl, formyl, sulphamoyl, hydroxyl, amino, halogen, C₁-C₄-alkyl, C₁-C₄-haloalkyl, C₁-C₄-alkoxy or C₁-C₄-haloalkoxy.

The formula (I) provides a general definition of the compounds according to the invention. Preferred substituents or ranges of the radicals listed in the formulae given above and below are illustrated below:

- X preferably represents chlorine or bromine,
- 25 Y preferably represents C₁-C₃-alkyl,
- Z preferably represents ethyl, n-propyl or n-butyl,

A, B and the carbon atom to which they are attached preferably represent saturated C₃-C₈-cycloalkyl in which optionally one methylene group is replaced by oxygen or sulphur and which is optionally substituted by C₁-C₄-haloalkyl or C₁-C₆-alkoxy,

G preferably represents hydrogen (a) or represents one of the groups



in which

E represents a metal ion equivalent or an ammonium ion,

5 L represents oxygen or sulphur and

M represents oxygen or sulphur,

R¹ preferably represents C₁-C₂₀-alkyl, C₂-C₂₀-alkenyl, C₁-C₆-alkoxy-C₁-C₆-alkyl, C₁-C₆-alkylthio-C₁-C₆-alkyl or poly-C₁-C₄-alkoxy-C₁-C₄-alkyl, each of which is optionally mono- to heptasubstituted by halogen, mono- or disubstituted by cyano, monosubstituted by COR¹³,
 10 C=N-OR¹³, CO₂R¹³ or $\text{CON} \begin{smallmatrix} \text{R}^{13} \\ \text{R}^{13'} \end{smallmatrix}$, or represents C₃-C₈-cycloalkyl which is optionally mono- to trisubstituted by halogen, C₁-C₄-alkyl or C₁-C₄-alkoxy and in which optionally one or two not directly adjacent methylene groups are replaced by oxygen and/or sulphur,

represents phenyl, phenyl-C₁-C₂-alkyl or phenyl-C₁-C₂-alkenyl, each of which is optionally mono- to trisubstituted by halogen, cyano, nitro, C₁-C₆-alkyl, C₁-C₆-alkoxy, C₁-C₆-haloalkyl, C₁-C₆-haloalkoxy, C₁-C₆-alkylthio, C₁-C₆-alkylsulphinyl or C₁-C₆-alkylsulphonyl,
 15

represents 5- or 6-membered hetaryl which is optionally mono- or disubstituted by halogen or C₁-C₆-alkyl and which contains one or two heteroatoms from the group consisting of oxygen, sulphur and nitrogen,

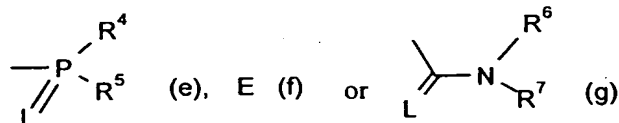
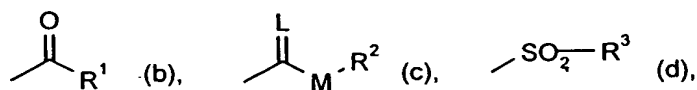
R² preferably represents C₁-C₂₀-alkyl, C₂-C₂₀-alkenyl, C₁-C₆-alkoxy-C₂-C₆-alkyl or poly-C₁-C₆-alkoxy-C₂-C₆-alkyl, each of which is optionally mono- to trisubstituted by halogen,
 20

represents C₃-C₈-cycloalkyl which is optionally mono- or disubstituted by halogen, C₁-C₆-alkyl or C₁-C₆-alkoxy or

represents phenyl or benzyl, each of which is optionally mono- to trisubstituted by halogen, cyano, nitro, C₁-C₆-alkyl, C₁-C₆-alkoxy, C₁-C₆-haloalkyl or C₁-C₆-haloalkoxy,

- R^3 preferably represents C_1 - C_8 -alkyl which is optionally mono- or polysubstituted by halogen or represents phenyl or benzyl, each of which is optionally mono- or disubstituted by halogen, C_1 - C_6 -alkyl, C_1 - C_6 -alkoxy, C_1 - C_4 -haloalkyl, C_1 - C_4 -haloalkoxy, cyano or nitro,
- 5 R^4 and R^5 independently of one another preferably represent C_1 - C_8 -alkyl, C_1 - C_8 -alkoxy, C_1 - C_8 -alkyl-amino, di- $(C_1$ - C_8 -alkyl)amino, C_1 - C_8 -alkylthio or C_2 - C_8 -alkenylthio, each of which is optionally mono- to trisubstituted by halogen, or represent phenyl, phenoxy or phenylthio, each of which is optionally mono- to trisubstituted by halogen, nitro, cyano, C_1 - C_4 -alkoxy, C_1 - C_4 -haloalkoxy, C_1 - C_4 -alkylthio, C_1 - C_4 -haloalkylthio, C_1 - C_4 -alkyl or C_1 - C_4 -haloalkyl,
- 10 R^6 and R^7 independently of one another preferably represent hydrogen, represent C_1 - C_8 -alkyl, C_3 - C_8 -cycloalkyl, C_1 - C_8 -alkoxy, C_3 - C_8 -alkenyl or C_1 - C_8 -alkoxy- C_2 - C_8 -alkyl, each of which is optionally mono- to trisubstituted by halogen, represent phenyl or benzyl, each of which is optionally mono- to trisubstituted by halogen, C_1 - C_8 -alkyl, C_1 - C_8 -haloalkyl or C_1 - C_8 -alkoxy, or together represent a C_3 - C_6 -alkylene radical which is optionally mono- or disubstituted by C_1 - C_4 -alkyl and in which optionally one methylene group is replaced by oxygen or sulphur,
- 15 R^{13} preferably represents C_1 - C_6 -alkyl, C_3 - C_6 -alkenyl, C_3 - C_6 -alkynyl or C_1 - C_4 -alkoxy- C_2 - C_4 -alkyl, each of which is optionally mono- to trisubstituted by halogen, or represents C_3 - C_6 -cycloalkyl which is optionally mono- or disubstituted by halogen, C_1 - C_2 -alkyl or C_1 - C_2 -alkoxy and in which optionally one or two not directly adjacent methylene groups are replaced by oxygen, or represents phenyl or phenyl- C_1 - C_2 -alkyl, each of which is
- 20 optionally mono- or disubstituted by halogen, C_1 - C_4 -alkyl, C_1 - C_4 -alkoxy, C_1 - C_2 -haloalkyl, C_1 - C_2 -haloalkoxy, cyano or nitro,
- R^{13} preferably represents hydrogen, C_1 - C_6 -alkyl or C_3 - C_6 -alkenyl.
- In the radical definitions mentioned as being preferred, halogen represents fluorine, chlorine, bromine and iodine, in particular fluorine, chlorine and bromine.
- 25 X particularly preferably represents chlorine or bromine,
- Y particularly preferably represents methyl or ethyl,
- Z particularly preferably represents ethyl or n-propyl,
- A, B and the carbon atom to which they are attached particularly preferably represent saturated C_3 - C_7 -cycloalkyl in which optionally one methylene group is replaced by oxygen and which
- 30 is optionally monosubstituted by C_1 - C_2 -haloalkyl or C_1 - C_4 -alkoxy,

G particularly preferably represents hydrogen (a) or represents one of the groups



in which

E represents a metal ion equivalent or an ammonium ion,

5 L represents oxygen or sulphur and

M represents oxygen or sulphur,

10 R^1 particularly preferably represents $\text{C}_1\text{-C}_{10}$ -alkyl, $\text{C}_2\text{-C}_{10}$ -alkenyl, $\text{C}_1\text{-C}_4$ -alkoxy- $\text{C}_1\text{-C}_2$ -alkyl, $\text{C}_1\text{-C}_4$ -alkylthio- $\text{C}_1\text{-C}_2$ -alkyl or poly- $\text{C}_1\text{-C}_3$ -alkoxy- $\text{C}_1\text{-C}_2$ -alkyl, each of which is optionally mono- to pentasubstituted by fluorine or chlorine, monosubstituted by cyano, monosubstituted by CO-R^{13} , C=N-OR^{13} or CO_2R^{13} , or represents $\text{C}_3\text{-C}_6$ -cycloalkyl which is optionally mono- or disubstituted by fluorine, chlorine, $\text{C}_1\text{-C}_2$ -alkyl or $\text{C}_1\text{-C}_2$ -alkoxy and in which optionally one or two not directly adjacent methylene groups are replaced by oxygen,

15 represents phenyl or benzyl, each of which is optionally mono- or disubstituted by fluorine, chlorine, bromine, cyano, nitro, $\text{C}_1\text{-C}_4$ -alkyl, $\text{C}_1\text{-C}_4$ -alkylthio, $\text{C}_1\text{-C}_4$ -alkylsulphinyl, $\text{C}_1\text{-C}_4$ -alkylsulphonyl, $\text{C}_1\text{-C}_4$ -alkoxy, $\text{C}_1\text{-C}_2$ -haloalkyl or $\text{C}_1\text{-C}_2$ -haloalkoxy,

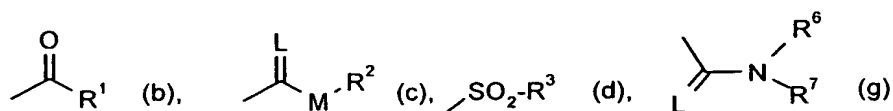
represents pyrazolyl, thiazolyl, pyridyl, pyrimidyl, furanyl or thienyl, each of which is optionally mono- or disubstituted by fluorine, chlorine, bromine or $\text{C}_1\text{-C}_2$ -alkyl,

20 R^2 particularly preferably represents $\text{C}_1\text{-C}_{10}$ -alkyl, $\text{C}_2\text{-C}_{10}$ -alkenyl, $\text{C}_1\text{-C}_4$ -alkoxy- $\text{C}_2\text{-C}_4$ -alkyl or poly- $\text{C}_1\text{-C}_4$ -alkoxy- $\text{C}_2\text{-C}_4$ -alkyl, each of which is optionally mono- to trisubstituted by fluorine or chlorine,

represents $\text{C}_3\text{-C}_7$ -cycloalkyl which is optionally monosubstituted by $\text{C}_1\text{-C}_2$ -alkyl or $\text{C}_1\text{-C}_2$ -alkoxy, or

represents phenyl or benzyl, each of which is optionally mono- or disubstituted by fluorine, chlorine, bromine, cyano, nitro, $\text{C}_1\text{-C}_4$ -alkyl, methoxy, trifluoromethyl or trifluoromethoxy,

- R³ particularly preferably represents C₁-C₄- alkyl which is optionally mono- to trisubstituted by fluorine or chlorine, or represents phenyl or benzyl, each of which is optionally monosubstituted by fluorine, chlorine, bromine, C₁-C₄-alkyl, C₁-C₄-alkoxy, trifluoromethyl, trifluoromethoxy, cyano or nitro,
- 5 R⁴ and R⁵ independently of one another each particularly preferably represent C₁-C₆-alkyl, C₁-C₆-alkoxy, C₁-C₆-alkylamino, di-(C₁-C₆-alkyl)amino, C₁-C₆-alkylthio or C₃-C₄-alkenylthio, each of which is optionally mono- to trisubstituted by fluorine or chlorine, or represent phenyl, phenoxy or phenylthio, each of which is optionally mono- or disubstituted by fluorine, chlorine, bromine, nitro, cyano, C₁-C₃-alkoxy, trifluoromethoxy, C₁-C₃-alkylthio, C₁-C₃-alkyl
- 10 or trifluoromethyl,
- R⁶ and R⁷ independently of one another particularly preferably represent hydrogen, represent C₁-C₆-alkyl, C₃-C₆-cycloalkyl, C₁-C₄-alkoxy, C₃-C₆-alkenyl or C₁-C₆-alkoxy-C₂-C₆-alkyl, each of which is optionally mono- to trisubstituted by fluorine or chlorine, represent phenyl which is optionally mono- or disubstituted by fluorine, chlorine, bromine, trifluoromethyl, C₁-C₄-alkyl
- 15 or C₁-C₄-alkoxy, or together represent a C₃-C₆-alkylene radical which is optionally mono- or disubstituted by methyl and in which optionally one methylene group is replaced by oxygen,
- R¹³ particularly preferably represents C₁-C₄-alkyl, C₃-C₄-alkenyl, C₃-C₄-alkynyl or C₁-C₄-alkoxy-C₂-C₃-alkyl or C₃-C₄-cycloalkyl in which optionally one methylene group is replaced by oxygen.
- 20 In the radical definitions mentioned as being particularly preferred, halogen represents fluorine, chlorine and bromine, in particular fluorine and chlorine.
- X very particularly preferably represents chlorine or bromine,
- Y very particularly preferably represents methyl,
- Z very particularly preferably represents ethyl,
- 25 A, B and the carbon atom to which they are attached very particularly preferably represent saturated C₆-cycloalkyl in which optionally one methylene group is replaced by oxygen and which is optionally monosubstituted by trifluoromethyl, methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy or isobutoxy,
- G very particularly preferably represents hydrogen (a) or represents one of the groups



in which

L represents oxygen and

M represents oxygen or sulphur,

- 5 R^1 very particularly preferably represents C_1 - C_6 -alkyl, C_2 - C_6 -alkenyl, C_1 - C_2 -alkoxy- C_1 - C_2 -alkyl, C_1 - C_2 -alkylthio- C_1 - C_2 -alkyl or poly- C_1 - C_2 -alkoxy- C_1 - C_2 -alkyl, each of which is optionally mono- to trisubstituted by fluorine or chlorine, or represents cyclopropyl, cyclopentyl or cyclohexyl, each of which is optionally monosubstituted by fluorine, chlorine, methyl, ethyl or methoxy,
- 10 represents phenyl which is optionally monosubstituted by fluorine, chlorine, bromine, cyano, nitro, methyl, ethyl, n-propyl, iso-propyl, methoxy, ethoxy, methylthio, ethylthio, methylsulphinyl, ethylsulphinyl, methylsulphonyl, ethylsulphonyl, trifluoromethyl or trifluoromethoxy,
- 15 represents furanyl, thienyl or pyridyl, each of which is optionally monosubstituted by chlorine, bromine or methyl,
- R^2 very particularly preferably represents C_1 - C_8 -alkyl, C_2 - C_6 -alkenyl or C_1 - C_3 -alkoxy- C_2 - C_3 -alkyl, cyclopentyl or cyclohexyl,
- or represents phenyl or benzyl, each of which is optionally monosubstituted by fluorine, chlorine, bromine, cyano, nitro, methyl, methoxy, trifluoromethyl or trifluoromethoxy,
- 20 R^3 very particularly preferably represents C_1 - C_4 -alkyl which is optionally mono- to trisubstituted by fluorine or chlorine or represents phenyl or benzyl, each of which is optionally monosubstituted by fluorine, chlorine, bromine, C_1 - C_4 -alkyl, C_1 - C_4 -alkoxy, trifluoromethyl, trifluoromethoxy, cyano or nitro,
- 25 R^6 very particularly preferably represents hydrogen, represents C_1 - C_4 -alkyl, C_3 - C_6 -cycloalkyl or allyl, represents phenyl which is optionally monosubstituted by fluorine, chlorine, bromine, methyl, methoxy or trifluoromethyl,
- R^7 very particularly preferably represents methyl, ethyl, n-propyl, isopropyl or allyl,

R^6 and R^7 together very particularly preferably represent a C_5 - C_6 -alkylene radical in which optionally one methylene group is replaced by oxygen.

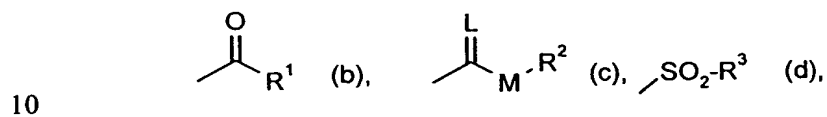
X especially represents chlorine or bromine,

Y especially represents methyl,

5 Z especially represents ethyl,

A, B and the carbon atom to which they are attached especially represent saturated C_6 -cycloalkyl in which optionally one methylene group is replaced by oxygen and which is optionally monosubstituted by methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy or isobutoxy,

G especially represents hydrogen (a) or represents one of the groups



in which

L represents oxygen and

M represents oxygen or sulphur,

15 R^1 especially represents C_1 - C_6 -alkyl, C_1 - C_2 -alkoxy- C_1 - C_2 -alkyl, each of which is optionally mono- to trisubstituted by fluorine or chlorine, or represents cyclopropyl,

R^2 especially represents C_1 - C_8 -alkyl or C_2 - C_6 -alkenyl,

R^3 especially represents C_1 - C_4 -alkyl.

The general or preferred radical definitions or illustrations listed above can be combined with one another as desired, i.e. including combinations between the respective ranges and preferred ranges.

20 They apply to the end products and, correspondingly, to the precursors and intermediates.

Preference according to the invention is given to the compounds of the formula (I) which contain a combination of the meanings listed above as being preferred (preferable).

Particular preference according to the invention is given to the compounds of the formula (I) which contain a combination of the meanings listed above as being particularly preferred.

Very particular preference according to the invention is given to the compounds of the formula (I) which contain a combination of the meanings listed above as being very particularly preferred.

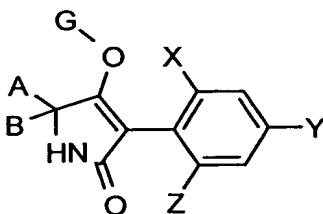
Especially preferred according to the invention are the compounds of the formula (I) which contain a combination of the meanings listed above as being especially preferred.

- 5 Saturated or unsaturated hydrocarbon radicals, such as alkyl, alkanediyl or alkenyl, can in each case be straight-chain or branched as far as this is possible, including in combination with heteroatoms, such as, for example, in alkoxy.

Optionally substituted radicals can be mono- or polysubstituted, where in the case of polysubstitution the substituents can be identical or different.

- 10 In addition to the compounds mentioned in the Preparation Examples, the following compounds of the formula (I-a) may be specifically mentioned:

Table 1:



G = H, X = Br, Y = CH₃, Z = C₂H₅

15

A	B
	-(CH ₂) ₂ -
	-(CH ₂) ₄ -
	-(CH ₂) ₅ -
	-(CH ₂) ₆ -
	-(CH ₂) ₇ -
	-(CH ₂) ₂ -O-(CH ₂) ₂ -
	-CH ₂ -O-(CH ₂) ₃ -
	-(CH ₂) ₂ -S-(CH ₂) ₂ -
	-(CH ₂) ₂ -CHOCH ₃ -(CH ₂) ₂ -
	-(CH ₂) ₂ -CHOC ₂ H ₅ -(CH ₂) ₂ -

A	B
	$-(\text{CH}_2)_2-\text{CHOC}_3\text{H}_7-(\text{CH}_2)_2-$
	$-(\text{CH}_2)_2-\text{CHOC}_4\text{H}_9-(\text{CH}_2)_2-$
	$-(\text{CH}_2)_2-\text{CH-O-i-C}_4\text{H}_9-(\text{CH}_2)_2-$

A, B, X, Y and Z are as stated in Table 1

	Table 2	$\text{G} = \text{CH}_3-\text{CO}$
	Table 3	$\text{G} = \text{C}_2\text{H}_5-\text{CO}$
5	Table 4	$\text{G} = \text{C}_3\text{H}_7-\text{CO}$
	Table 5	$\text{G} = \text{i-C}_3\text{H}_7-\text{CO}$
	Table 6	$\text{G} = \text{C}_4\text{H}_9-\text{CO}$
	Table 7	$\text{G} = \text{i-C}_4\text{H}_9-\text{CO}$
	Table 8	$\text{G} = \text{s-C}_4\text{H}_9-\text{CO}$
10	Table 9	$\text{G} = \text{t-C}_4\text{H}_9-\text{CO}$
	Table 10	$\text{G} = \triangle-\text{CO}$
	Table 11	$\text{G} = \text{H}_3\text{C-O-CH}_2-\text{CO}$
	Table 12	$\text{G} = \text{H}_5\text{C}_2-\text{O-CH}_2-\text{CO}$
	Table 13	$\text{G} = \text{H}_3\text{C-S-CH}_2-\text{CO}$
15	Table 14	$\text{G} = \text{H}_5\text{C}_2-\text{S-CH}_2-\text{CO}$
	Table 15	$\text{G} = \text{CH}_3-\text{O-CO}$
	Table 16	$\text{G} = \text{C}_2\text{H}_5-\text{O-CO}$
	Table 17	$\text{G} = \text{C}_3\text{H}_7-\text{O-CO}$
	Table 18	$\text{G} = \text{i-C}_3\text{H}_7-\text{O-CO}$
20	Table 19	$\text{G} = \text{C}_4\text{H}_9-\text{O-CO}$
	Table 20	$\text{G} = \text{i-C}_4\text{H}_9-\text{O-CO}$
	Table 21	$\text{G} = \text{s-C}_4\text{H}_9-\text{O-CO}$
	Table 22	$\text{G} = \text{t-C}_4\text{H}_9-\text{O-CO}$
	Table 23	$\text{G} = \text{t-C}_4\text{H}_9-\text{CH}_2-\text{O-CO}$
25	Table 24	$\text{G} = \text{C}_6\text{H}_5-\text{CH}_2-\text{O-CO}$
	Table 25	$\text{G} = \text{C}_6\text{H}_5-\text{O-CO}$
	Table 26	$\text{G} = \text{CH}_3-\text{S-CO}$
	Table 27	$\text{G} = \text{C}_2\text{H}_5-\text{S-CO}$
	Table 28	$\text{G} = \text{C}_3\text{H}_7-\text{S-CO}$
30	Table 29	$\text{G} = \text{i-C}_3\text{H}_7-\text{S-CO}$

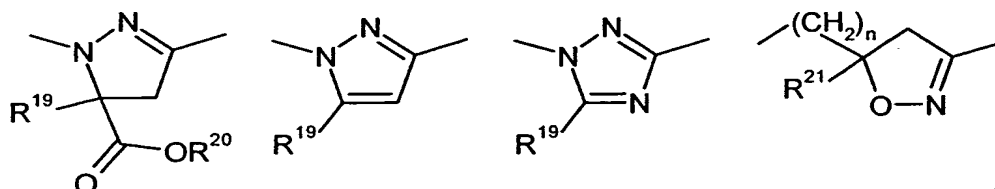
	Table 30	$G = C_4H_9-S-CO$
	Table 31	$G = i-C_4H_9-S-CO$
	Table 32	$G = s-C_4H_9-S-CO$
	Table 33	$G = t-C_4H_9-S-CO$
5	Table 34	$G = t-C_4H_9-CH_2-S-CO$
	Table 35	$G = C_6H_5-CH_2-S-CO$
	Table 36	A and B are as stated in Table 1 and $G = H, X = Cl; Y = CH_3; Z = C_2H_5.$
10	A and B are as stated in Table 1 and X, Y and Z are as stated in Table 36	
	Table 37	$G = CH_3-CO$
	Table 38	$G = C_2H_5-CO$
	Table 39	$G = C_3H_7-CO$
	Table 40	$G = i-C_3H_7-CO$
15	Table 41	$G = C_4H_9-CO$
	Table 42	$G = i-C_4H_9-CO$
	Table 43	$G = s-C_4H_9-CO$
	Table 44	$G = t-C_4H_9-CO$
	Table 45	$G = \triangle-CO$
20	Table 46	$G = H_3C-O-CH_2-CO$
	Table 47	$G = H_5C_2-O-CH_2-CO$
	Table 48	$G = H_3C-S-CH_2-CO$
	Table 49	$G = H_5C_2-S-CH_2-CO$
	Table 50	$G = CH_3-O-CO$
25	Table 51	$G = C_2H_5-O-CO$
	Table 52	$G = C_3H_7-O-CO$
	Table 53	$G = i-C_3H_7-O-CO$
	Table 54	$G = C_4H_9-O-CO$
	Table 55	$G = i-C_4H_9-O-CO$
30	Table 56	$G = s-C_4H_9-O-CO$
	Table 57	$G = t-C_4H_9-O-CO$
	Table 58	$G = t-C_4H_9-CH_2-O-CO$
	Table 59	$G = C_6H_5-CH_2-O-CO$
	Table 60	$G = C_6H_5-O-CO$

	Table 61	$G = \text{CH}_3\text{-S-CO}$
	Table 62	$G = \text{C}_2\text{H}_5\text{-S-CO}$
	Table 63	$G = \text{C}_3\text{H}_7\text{-S-CO}$
	Table 64	$G = \text{i-C}_3\text{H}_7\text{-S-CO}$
5	Table 65	$G = \text{C}_4\text{H}_9\text{-S-CO}$
	Table 66	$G = \text{i-C}_4\text{H}_9\text{-S-CO}$
	Table 67	$G = \text{s-C}_4\text{H}_9\text{-S-CO}$
	Table 68	$G = \text{t-C}_4\text{H}_9\text{-S-CO}$
	Table 69	$G = \text{t-C}_4\text{H}_9\text{-CH}_2\text{-S-CO}$
10	Table 70	$G = \text{C}_6\text{H}_5\text{-CH}_2\text{-S-CO}$

Preferred meanings of the groups listed above in connection with the crop plant compatibility-improving compounds ("herbicide safeners") of the formulae (IIa), (IIb), (IIc), (IId) and (IIe) are defined below.

15 m preferably represents the number 0, 1, 2, 3 or 4,

A^1 preferably represents one of the divalent heterocyclic groupings shown below



n preferably represents the number 0, 1, 2, 3 or 4.

20 A^2 preferably represents in each case optionally methyl-, ethyl-, methoxycarbonyl-, ethoxycarbonyl- or allyloxycarbonyl-substituted methylene or ethylene.

R^{14} preferably represents hydroxyl, mercapto, amino, methoxy, ethoxy, n- or i-propoxy, n-, i-, s- or t-butoxy, methylthio, ethylthio, n- or i-propylthio, n-, i-, s- or t-butylthio, methylamino, ethylamino, n- or i-propylamino, n-, i-, s- or t-butylamino, dimethylamino or diethylamino.

25 R^{15} preferably represents hydroxyl, mercapto, amino, methoxy, ethoxy, n- or i-propoxy, n-, i-, s- or t-butoxy, 1-methylhexyloxy, allyloxy, 1-allyloxymethylethoxy, methylthio, ethylthio, n- or i-propylthio, n-, i-, s- or t-butylthio, methylamino, ethylamino, n- or i-propylamino, n-, i-, s- or t-butylamino, dimethylamino or diethylamino.

- R¹⁶ preferably represents in each case optionally fluorine-, chlorine- and/or bromine-substituted methyl, ethyl, n- or i-propyl.
- 5 R¹⁷ preferably represents hydrogen, in each case optionally fluorine- and/or chlorine-substituted methyl, ethyl, n- or i-propyl, n-, i-, s- or t-butyl, propenyl, butenyl, propynyl or butynyl, methoxymethyl, ethoxymethyl, methoxyethyl, ethoxyethyl, dioxolanylemethyl, furyl, furyl-methyl, thienyl, thiazolyl, piperidinyl, or optionally fluorine-, chlorine-, methyl-, ethyl-, n- or i-propyl-, n-, i-, s- or t-butyl-substituted phenyl.
- 10 R¹⁸ preferably represents hydrogen, in each case optionally fluorine- and/or chlorine-substituted methyl, ethyl, n- or i-propyl, n-, i-, s- or t-butyl, propenyl, butenyl, propynyl or butynyl, methoxymethyl, ethoxymethyl, methoxyethyl, ethoxyethyl, dioxolanylemethyl, furyl, furyl-methyl, thienyl, thiazolyl, piperidinyl, or optionally fluorine-, chlorine-, methyl-, ethyl-, n- or i-propyl-, n-, i-, s- or t-butyl-substituted phenyl, or together with R¹⁷ represents one of the radicals $-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-$ and $-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-$ which are optionally substituted by methyl, ethyl, furyl, phenyl, a fused benzene ring or by two substituents which, together with the C atom to which they are attached, form a 5- or 6-membered carbocycle.
- 15 R¹⁹ preferably represents hydrogen, cyano, fluorine, chlorine, bromine, or represents in each case optionally, fluorine-, chlorine- and/or bromine-substituted methyl, ethyl, n- or i-propyl, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl or phenyl.
- 20 R²⁰ preferably represents hydrogen, optionally hydroxyl-, cyano-, fluorine-, chlorine-, methoxy-, ethoxy-, n- or i-propoxy-substituted methyl, ethyl, n- or i-propyl, n-, i-, s- or t-butyl.
- R²¹ preferably represents hydrogen, cyano, fluorine, chlorine, bromine, or represents in each case optionally fluorine-, chlorine- and/or bromine-substituted methyl, ethyl, n- or i-propyl, n-, i-, s- or t-butyl, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl or phenyl.
- 25 X¹ preferably represents nitro, cyano, fluorine, chlorine, bromine, methyl, ethyl, n- or i-propyl, n-, i-, s- or t-butyl, difluoromethyl, dichloromethyl, trifluoromethyl, trichloromethyl, chloro-difluoromethyl, fluorodichloromethyl, methoxy, ethoxy, n- or i-propoxy, difluoromethoxy or trifluoromethoxy.
- 30 X² preferably represents hydrogen, nitro, cyano, fluorine, chlorine, bromine, methyl, ethyl, n- or i-propyl, n-, i-, s- or t-butyl, difluoromethyl, dichloromethyl, trifluoromethyl, trichloromethyl, chlorodifluoromethyl, fluorodichloromethyl, methoxy, ethoxy, n- or i-propoxy, difluoromethoxy or trifluoromethoxy.

- X^3 preferably represents hydrogen, nitro, cyano, fluorine, chlorine, bromine, methyl, ethyl, n- or i-propyl, n-, i-, s- or t-butyl, difluoromethyl, dichloromethyl, trifluoromethyl, trichloromethyl, chlorodifluoromethyl, fluorodichloromethyl, methoxy, ethoxy, n- or i-propoxy, difluoromethoxy or trifluoromethoxy.
- 5 t preferably represents the number 0, 1, 2, 3 or 4.
- v preferably represents the number 0, 1, 2 or 3.
- R^{22} preferably represents hydrogen, methyl, ethyl, n- or i-propyl.
- R^{23} preferably represents hydrogen, methyl, ethyl, n- or i-propyl.
- 10 R^{24} preferably represents hydrogen, in each case optionally cyano-, fluorine-, chlorine-, methoxy-, ethoxy-, n- or i-propoxy-substituted methyl, ethyl, n- or i-propyl, n-, i-, s- or t-butyl, methoxy, ethoxy, n- or i-propoxy, n-, i-, s- or t-butoxy, methylthio, ethylthio, n- or i-propylthio, n-, i-, s- or t-butylthio, methylamino, ethylamino, n- or i-propylamino, n-, i-, s- or t-butylamino, dimethylamino or diethylamino, or in each case optionally cyano-, fluorine-, chlorine-, bromine-, methyl-, ethyl-, n- or i-propyl-substituted cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cyclopropyloxy, cyclobutyloxy, cyclopentyloxy, cyclohexyloxy, cyclopropylthio, cyclobutylthio, cyclopentylthio, cyclohexylthio, cyclopropylamino, cyclobutylamino, cyclopentylamino or cyclohexylamino.
- 15 R^{25} preferably represents hydrogen, in each case optionally cyano-, hydroxyl-, fluorine-, chlorine-, methoxy-, ethoxy-, n- or i-propoxy-substituted methyl, ethyl, n- or i-propyl, n-, i- or s-butyl, in each case optionally cyano-, fluorine-, chlorine- or bromine-substituted propenyl, butenyl, propynyl or butynyl, or in each case optionally cyano-, fluorine-, chlorine-, bromine-, methyl-, ethyl-, n- or i-propyl-substituted cyclopropyl, cyclobutyl, cyclopentyl or cyclohexyl.
- 20 R^{26} preferably represents hydrogen, in each case optionally cyano-, hydroxyl-, fluorine-, chlorine-, methoxy-, ethoxy-, n- or i-propoxy-substituted methyl, ethyl, n- or i-propyl, n-, i- or s-butyl, in each case optionally cyano-, fluorine-, chlorine- or bromine-substituted propenyl, butenyl, propynyl or butynyl, in each case optionally cyano-, fluorine-, chlorine-, bromine-, methyl-, ethyl-, n- or i-propyl-substituted cyclopropyl, cyclobutyl, cyclopentyl or cyclohexyl, or optionally nitro-, cyano-, fluorine-, chlorine-, bromine-, methyl-, ethyl-, n- or i-propyl-, n-, i-, s- or t-butyl-, trifluoromethyl-, methoxy-, ethoxy-, n- or i-propoxy-, difluoromethoxy- or trifluoromethoxy-substituted phenyl, or together with R^{25} represents in each case optionally
- 25 R^{26} preferably represents hydrogen, in each case optionally cyano-, hydroxyl-, fluorine-, chlorine-, methoxy-, ethoxy-, n- or i-propoxy-substituted methyl, ethyl, n- or i-propyl, n-, i- or s-butyl, in each case optionally cyano-, fluorine-, chlorine- or bromine-substituted propenyl, butenyl, propynyl or butynyl, in each case optionally cyano-, fluorine-, chlorine-, bromine-, methyl-, ethyl-, n- or i-propyl-substituted cyclopropyl, cyclobutyl, cyclopentyl or cyclohexyl, or optionally nitro-, cyano-, fluorine-, chlorine-, bromine-, methyl-, ethyl-, n- or i-propyl-, n-, i-, s- or t-butyl-, trifluoromethyl-, methoxy-, ethoxy-, n- or i-propoxy-, difluoromethoxy- or trifluoromethoxy-substituted phenyl, or together with R^{25} represents in each case optionally
- 30 R^{26} preferably represents hydrogen, in each case optionally cyano-, hydroxyl-, fluorine-, chlorine-, methoxy-, ethoxy-, n- or i-propoxy-substituted methyl, ethyl, n- or i-propyl, n-, i- or s-butyl, in each case optionally cyano-, fluorine-, chlorine- or bromine-substituted propenyl, butenyl, propynyl or butynyl, in each case optionally cyano-, fluorine-, chlorine-, bromine-, methyl-, ethyl-, n- or i-propyl-substituted cyclopropyl, cyclobutyl, cyclopentyl or cyclohexyl, or optionally nitro-, cyano-, fluorine-, chlorine-, bromine-, methyl-, ethyl-, n- or i-propyl-, n-, i-, s- or t-butyl-, trifluoromethyl-, methoxy-, ethoxy-, n- or i-propoxy-, difluoromethoxy- or trifluoromethoxy-substituted phenyl, or together with R^{25} represents in each case optionally

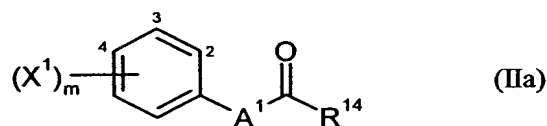
methyl- or ethyl-substituted butane-1,4-diyl (trimethylene), pentane-1,5-diyl, 1-oxabutane-1,4-diyl or 3-oxapentane-1,5-diyl.

5 X^4 preferably represents nitro, cyano, carboxyl, carbamoyl, formyl, sulphamoyl, hydroxyl, amino, fluorine, chlorine, bromine, methyl, ethyl, n- or i-propyl, n-, i-, s- or t-butyl, trifluoromethyl, methoxy, ethoxy, n- or i-propoxy, difluoromethoxy or trifluoromethoxy.

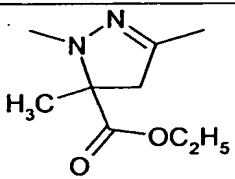
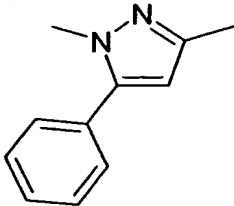
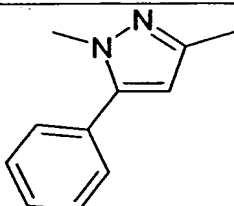
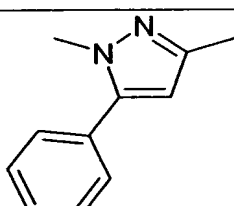
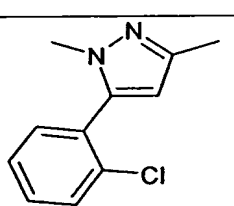
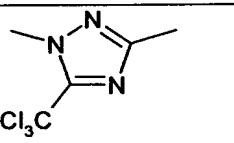
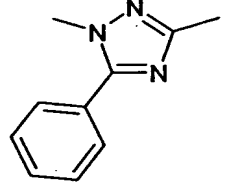
X^5 preferably represents nitro, cyano, carboxyl, carbamoyl, formyl, sulphamoyl, hydroxyl, amino, fluorine, chlorine, bromine, methyl, ethyl, n- or i-propyl, n-, i-, s- or t-butyl, trifluoromethyl, methoxy, ethoxy, n- or i-propoxy, difluoromethoxy or trifluoromethoxy.

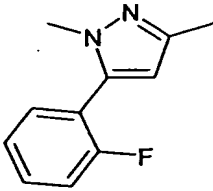
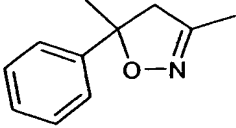
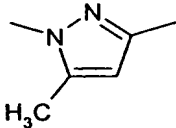
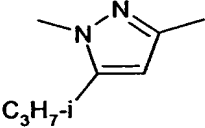
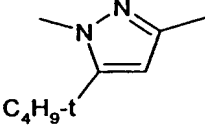
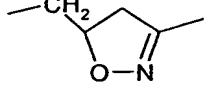
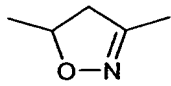
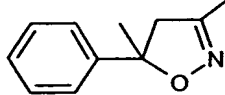
10 Examples of the compounds of the formula (IIa) which are very particularly preferred as herbicide safeners according to the invention are listed in Table 2 below.

Table 2: Examples of the compounds of the formula (IIa)

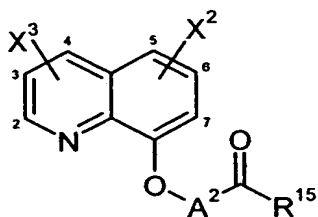


Example No.	(positions) $(X^1)_m$	A^1	R^{14}
IIa-1	(2) Cl, (4) Cl		OCH_3
IIa-2	(2) Cl, (4) Cl		OCH_3
IIa-3	(2) Cl, (4) Cl		OC_2H_5

Example No.	(positions) $(X^I)_m$	A^I	R^{14}
IIa-4	(2) Cl, (4) Cl		OC_2H_5
IIa-5	(2) Cl		OCH_3
IIa-6	(2) Cl, (4) Cl		OCH_3
IIa-7	(2) F		OCH_3
IIa-8	(2) F		OCH_3
IIa-9	(2) Cl, (4) Cl		OC_2H_5
IIa-10	(2) Cl, (4) CF_3		OCH_3

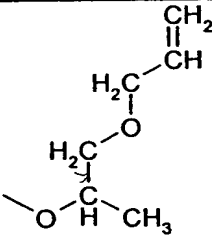
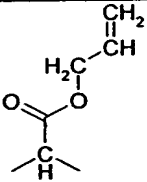
Example No.	(positions) $(X^1)_m$	A^1	R^{14}
IIa-11	(2) Cl		OCH_3
IIa-12	-		OC_2H_5
IIa-13	(2) Cl, (4) Cl		OC_2H_5
IIa-14	(2) Cl, (4) Cl		OC_2H_5
IIa-15	(2) Cl, (4) Cl		OC_2H_5
IIa-16	(2) Cl, (4) Cl		OC_2H_5
IIa-17	(2) Cl, (4) Cl		OC_2H_5
IIa-18	-		OH

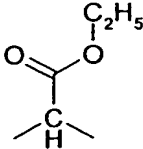
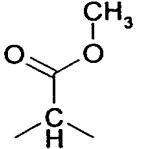
Examples of the compounds of the formula (IIb) which are very particularly preferred as herbicide safeners according to the invention are listed in Table 3 below.



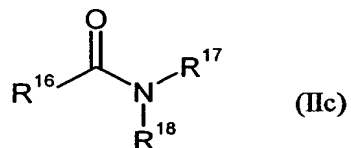
(IIb)

Table 3: Examples of the compounds of the formula (IIb)

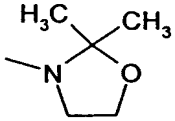
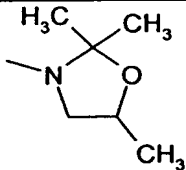
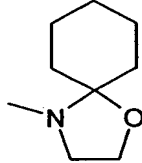
Example No.	(position) X^2	(position) X^3	A^2	R^{15}
IIb-1	(5) Cl	-	CH_2	OH
IIb-2	(5) Cl	-	CH_2	OCH_3
IIb-3	(5) Cl	-	CH_2	OC_2H_5
IIb-4	(5) Cl	-	CH_2	OC_3H_7-n
IIb-5	(5) Cl	-	CH_2	OC_3H_7-i
IIb-6	(5) Cl	-	CH_2	OC_4H_9-n
IIb-7	(5) Cl	-	CH_2	$OCH(CH_3)C_5H_{11-n}$
IIb-8	(5) Cl	(2) F	CH_2	OH
IIb-9	(5) Cl	(2) Cl	CH_2	OH
IIb-10	(5) Cl	-	CH_2	$OCH_2CH=CH_2$
IIb-11	(5) Cl	-	CH_2	OC_4H_9-i
IIb-12	(5) Cl	-	CH_2	
IIb-13	(5) Cl	-		$OCH_2CH=CH_2$

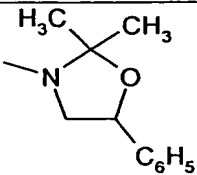
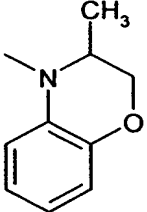
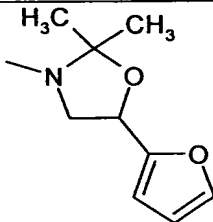
Example No.	(position) X^2	(position) X^3	A^2	R^{15}
IIb-14	(5) Cl	-		OC_2H_5
IIb-15	(5) Cl	-		OCH_3

Examples of the compounds of the formula (IIc) which are very particularly preferred as herbicide safeners according to the invention are listed in Table 4 below.



5 **Table 4:** Examples of the compounds of the formula (IIc)

Example No.	R^{16}	$N(R^{17}, R^{18})$
IIc-1	$CHCl_2$	$N(CH_2CH=CH_2)_2$
IIc-2	$CHCl_2$	
IIc-3	$CHCl_2$	
IIc-4	$CHCl_2$	

Example No.	R ¹⁶	N(R ¹⁷ , R ¹⁸)
IIc-5	CHCl ₂	
IIc-6	CHCl ₂	
IIc-7	CHCl ₂	

Examples of the compounds of the formula (II_d) which are very particularly preferred as herbicide safeners according to the invention are listed in Table 5 below.

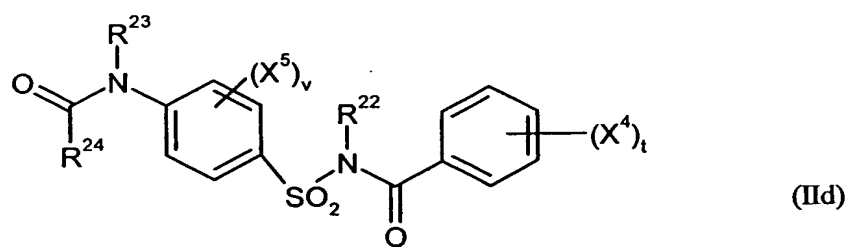



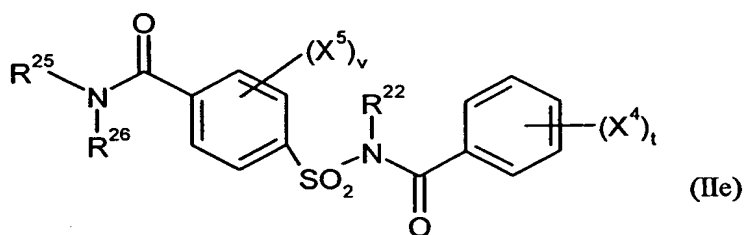


Table 5: Examples of the compounds of the formula (II d)


Example No.	R ²²	R ²³	R ²⁴	(positions) (X ⁴) _i	(positions) (X ⁵) _v
II d-1	H	H	CH ₃	(2) OCH ₃	-
II d-2	H	H	C ₂ H ₅	(2) OCH ₃	-
II d-3	H	H	C ₃ H _{7-n}	(2) OCH ₃	-
II d-4	H	H	C ₃ H _{7-i}	(2) OCH ₃	-
II d-5	H	H		(2) OCH ₃	-
II d-6	H	H	CH ₃	(2) OCH ₃ (5) CH ₃	-
II d-7	H	H	C ₂ H ₅	(2) OCH ₃ (5) CH ₃	-
II d-8	H	H	C ₃ H _{7-n}	(2) OCH ₃ (5) CH ₃	-
II d-9	H	H	C ₃ H _{7-i}	(2) OCH ₃ (5) CH ₃	-
II d-10	H	H		(2) OCH ₃ (5) CH ₃	-
II d-11	H	H	OCH ₃	(2) OCH ₃ (5) CH ₃	-
II d-12	H	H	OC ₂ H ₅	(2) OCH ₃ (5) CH ₃	-
II d-13	H	H	OC ₃ H _{7-i}	(2) OCH ₃ (5) CH ₃	-
II d-14	H	H	SCH ₃	(2) OCH ₃ (5) CH ₃	-
II d-15	H	H	SC ₂ H ₅	(2) OCH ₃ (5) CH ₃	-
II d-16	H	H	SC ₃ H _{7-i}	(2) OCH ₃ (5) CH ₃	-
II d-17	H	H	NHCH ₃	(2) OCH ₃ (5) CH ₃	-


Example No.	R ²²	R ²³	R ²⁴	(positions) (X ⁴) _t	(positions) (X ⁵) _v
II-d-18	H	H	NHC ₂ H ₅	(2) OCH ₃ (5) CH ₃	-
II-d-19	H	H	NHC ₃ H _{7-i}	(2) OCH ₃ (5) CH ₃	-
II-d-20	H	H		(2) OCH ₃ (5) CH ₃	-
II-d-21	H	H	NHCH ₃	(2) OCH ₃	-
II-d-22	H	H	NHC ₃ H _{7-i}	(2) OCH ₃	-
II-d-23	H	H	N(CH ₃) ₂	(2) OCH ₃	-
II-d-24	H	H	N(CH ₃) ₂	(3) CH ₃ (4) CH ₃	-
II-d-25	H	H	CH ₂ -O-CH ₃	(2) OCH ₃	-

Examples of the compounds of the formula (IIe) which are very particularly preferred as herbicide safeners according to the invention are listed in Table 6 below.



5 **Table 6:** Examples of the compounds of the formula (IIe)

Example No.	R ²²	R ²⁵	R ²⁶	(positions) (X ⁴) _t	(positions) (X ⁵) _v
IIe-1	H	H	CH ₃	(2) OCH ₃	-
IIe-2	H	H	C ₂ H ₅	(2) OCH ₃	-
IIe-3	H	H	C ₃ H _{7-n}	(2) OCH ₃	-
IIe-4	H	H	C ₃ H _{7-i}	(2) OCH ₃	-
IIe-5	H	H		(2) OCH ₃	-
IIe-6	H	CH ₃	CH ₃	(2) OCH ₃	-

Example No.	R ²²	R ²⁵	R ²⁶	(positions) (X ⁴) _t	(positions) (X ⁵) _v
IIe-7	H	H	CH ₃	(2) OCH ₃ (5) CH ₃	-
IIe-8	H	H	C ₂ H ₅	(2) OCH ₃ (5) CH ₃	-
IIe-9	H	H	C ₃ H _{7-n}	(2) OCH ₃ (5) CH ₃	-
IIe-10	H	H	C ₃ H _{7-i}	(2) OCH ₃ (5) CH ₃	-
IIe-11	H	H		(2) OCH ₃ (5) CH ₃	-
IIe-12	H	CH ₃	CH ₃	(2) OCH ₃ (5) CH ₃	-

Most preferred as crop plant compatibility-improving compounds [component (b)] are cloquintocet-mexyl, fenchlorazole-ethyl, isoxadifen-ethyl, mefenpyr-diethyl, furilazole, fenclorim, cumyluron, dymron, dimepiperate and the compounds IIe-5 and IIe-11, and particular emphasis is given to

5 cloquintocet-mexyl and mefenpyr-diethyl.

The compounds of the general formula (IIa) to be used as safeners according to the invention are known and/or can be prepared by processes known per se (cf. WO-A-91/07874, WO-A-95/07897).

The compounds of the general formula (IIb) to be used as safeners according to the invention are known and/or can be prepared by processes known per se (cf. EP-A-191736).

10 The compounds of the general formula (IIc) to be used as safeners according to the invention are known and/or can be prepared by processes known per se (cf. DE-A-2218097, DE-A-2350547).

The compounds of the general formula (IId) to be used as safeners according to the invention are known and/or can be prepared by processes known per se (cf. DE-A-19621522/US-A-6235680).

15 The compounds of the general formula (IIe) to be used as safeners according to the invention are known and can be prepared by processes known per se (cf. WO-A-99/66795/US-A-6251827).

Examples of the selective herbicidal combinations according to the invention comprising in each case one active compound of the formula (I) and one of the safeners defined above are listed in Table 7 below.

Table 7: Examples of the combinations according to the invention

Active compounds of the formula (I)	Safeners
I-a	cloquintocet-mexyl
I-a	fenchlorazole-ethyl
I-a	isoxadifen-ethyl
I-a	mefenpyr-diethyl
I-a	furilazole
I-a	fenclorim
I-a	cumyluron
I-a	daimuron /dymron
I-a	dimepiperate
I-a	Ile-11
I-a	Ile-5
I-b	cloquintocet-mexyl
I-b	fenchlorazole-ethyl
I-b	isoxadifen-ethyl
I-b	mefenpyr-diethyl
I-b	furilazole
I-b	fenclorim
I-b	cumyluron
I-b	daimuron /dymron
I-b	dimepiperate
I-b	Ile-11
I-b	Ile-5
I-c	cloquintocet-mexyl
I-c	fenchlorazole-ethyl
I-c	isoxadifen-ethyl
I-c	mefenpyr-diethyl
I-c	furilazole
I-c	fenclorim
I-c	cumyluron
I-c	daimuron /dymron
I-c	dimepiperate
I-c	Ile-5

I-c	Ile-11
I-d	cloquintocet-mexyl
I-d	fenchlorazole-ethyl
I-d	isoxadifen-ethyl
I-d	mefenpyr-diethyl
I-d	furilazole
I-d	fenclorim
I-d	cumyluron
I-d	daimuron /dymron
I-d	dimepiperate
I-d	Ile-11
I-d	Ile-5
I-e	cloquintocet-mexyl
I-e	fenchlorazole-ethyl
I-e	isoxadifen-ethyl
I-e	mefenpyr-diethyl
I-e	furilazole
I-e	fenclorim
I-e	cumyluron
I-e	daimuron /dymron
I-e	dimepiperate
I-e	Ile-5
I-e	Ile-11
I-f	cloquintocet-mexyl
I-f	fenchlorazole-ethyl
I-f	isoxadifen-ethyl
I-f	mefenpyr-diethyl
I-f	furilazole
I-f	fenclorim
I-f	cumyluron
I-f	daimuron /dymron
I-f	dimepiperate
I-f	Ile-5
I-f	Ile-11
I-g	cloquintocet-mexyl

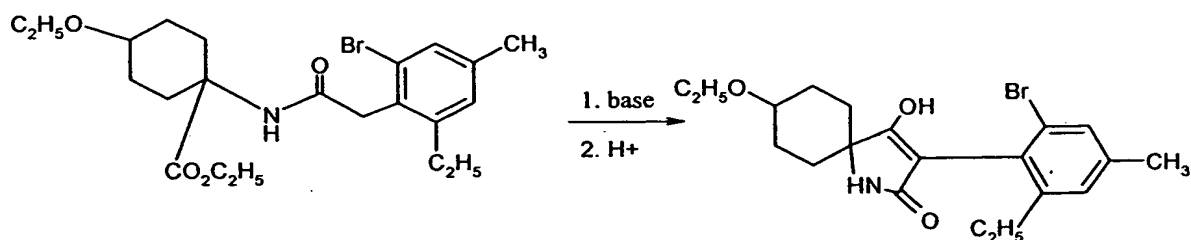
I-g	fenchlorazole-ethyl
I-f	isoxadifen-ethyl
I-g	mefenpyr-diethyl
I-g	furilazole
I-g	fenclozim
I-g	cumyluron
I-g	daimuron /dymron
I-g	dimepiperate
I-g	Ile-5
I-g	Ile-11

Surprisingly, it has now been found that the active compound combinations defined above of substituted cyclic ketoenols of the general formula (I) and safeners (antidotes) from the group (b') listed above, while having very good compatibility with useful plants, have a particularly high herbicidal activity and can be used in various crops, in particular in cereals (especially wheat), but also in soybeans, potatoes, maize and rice, for the selective control of weeds.

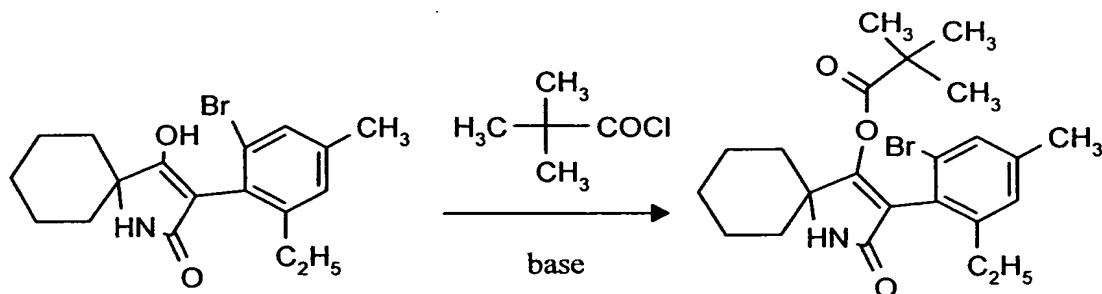
Here, it has to be considered to be surprising that, from the large number of known safeners or antidotes capable of antagonizing the damaging effect of a herbicide on the crop plants, it is in particular the compounds of group (b') listed above which are suitable to compensate the damaging effect of substituted cyclic ketoenols on the crop plants almost completely, without negatively affecting the herbicidal activity against the weeds to any considerable extent.

Emphasis may be given here to the particularly advantageous effect of the particularly preferred and most preferred combination partners from group (b'), in particular with respect to sparing cereal plants, such as, for example, wheat, barley and rye, but also maize and rice, as crop plants.

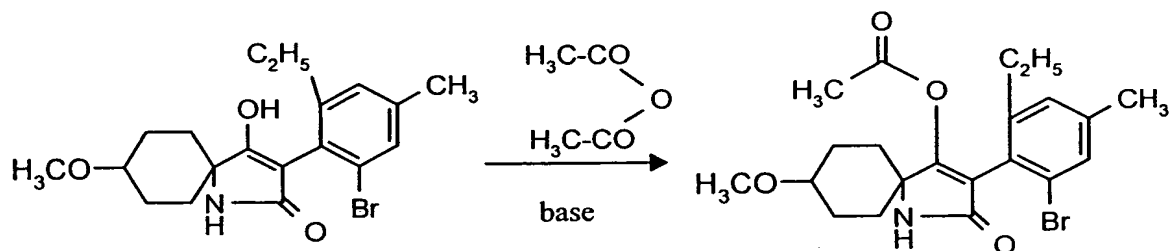
Using, for example, according to process (A) ethyl N-[(2-bromo-4-methyl-6-ethyl)phenylacetyl]-1-amino-4-ethoxycyclohexanecarboxylate as starting material, the course of the process according to the invention can be represented by the reaction scheme below:



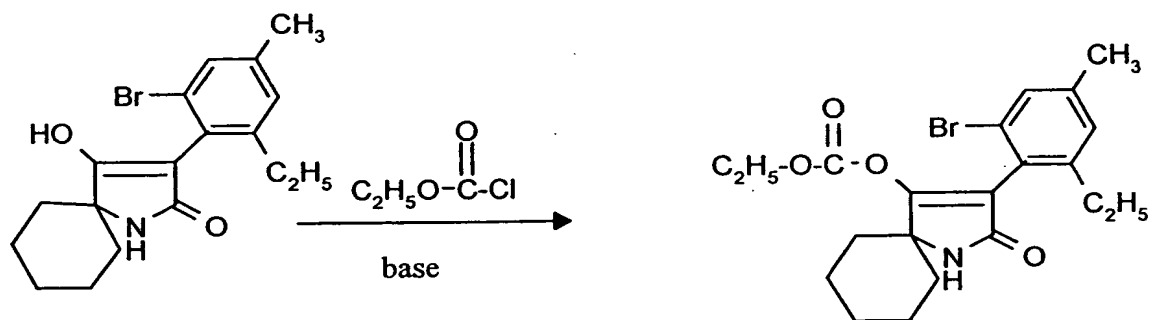
Using, for example, according to process (Ba) 3-[(2-bromo-4-methyl-6-ethyl)phenyl]-1-azaspiro[4,5]decane-2,4-dione and pivaloyl chloride as starting materials, the course of the process according to the invention can be represented by the reaction scheme below:



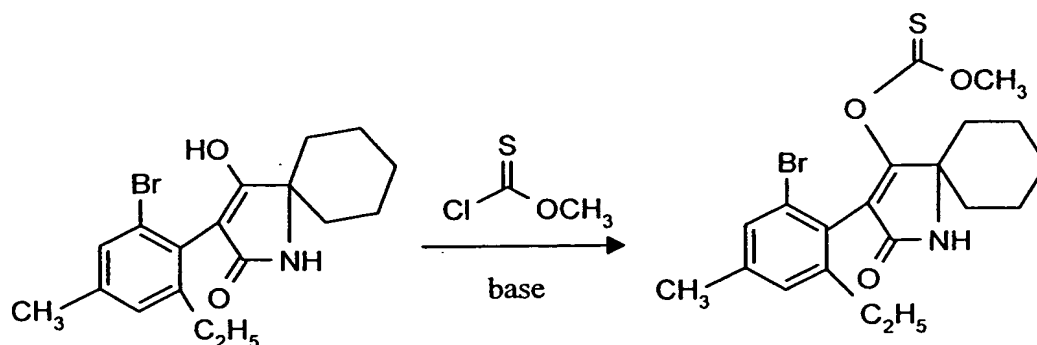
- 5 Using, for example, according to process (B) (variant β) 8-methoxy-3-[(2-bromo-4-methyl-6-ethyl)phenyl]-1-azaspiro[4,5]decane-2,4-dione and acetic anhydride as starting materials, the course of the process according to the invention can be represented by the reaction scheme below:



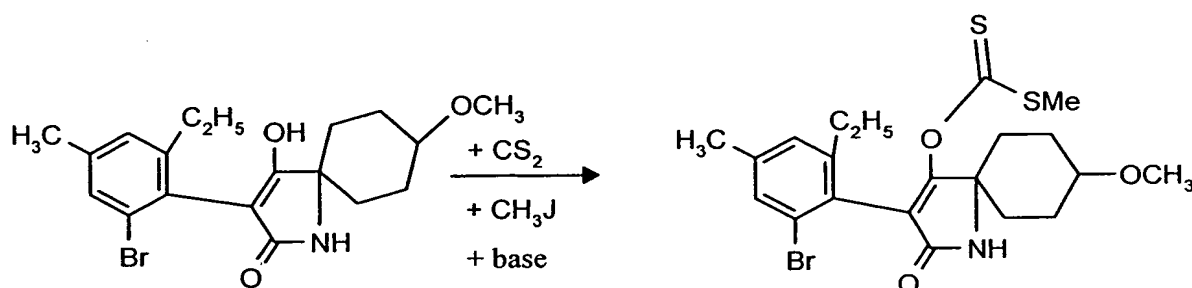
- 10 Using, for example, according to process (C) 3-[(2-bromo-4-methyl-6-ethyl)phenyl]-1-azaspiro[4,5]decane-2,4-dione and ethyl chloroformate as starting materials, the course of the process according to the invention can be represented by the reaction scheme below:



- 15 Using, for example, according to process (D), variant α , 3-[(2-bromo-4-methyl-6-ethyl)phenyl]-1-azaspiro[4,5]decane-2,4-dione and methyl chloromonothioformate as starting materials, the course of the reaction can be represented as follows:

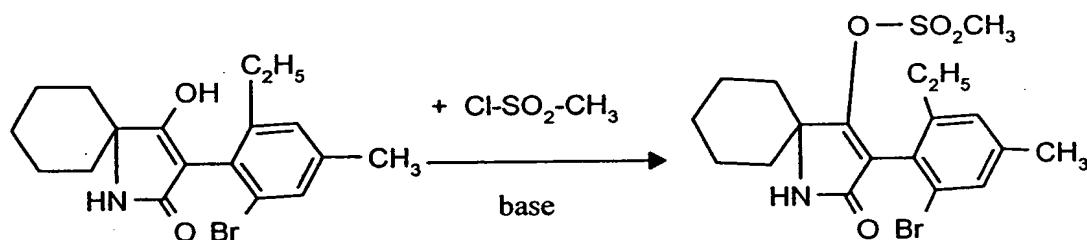


Using, for example, according to process (D), variant B, 8-methoxy-3-[(2-bromo-4-methyl-6-ethyl)-phenyl]-1-azaspiro[4,5]decane-2,4-dione, carbon disulphide and methyl iodide as starting materials, the course of the reaction can be represented as follows:

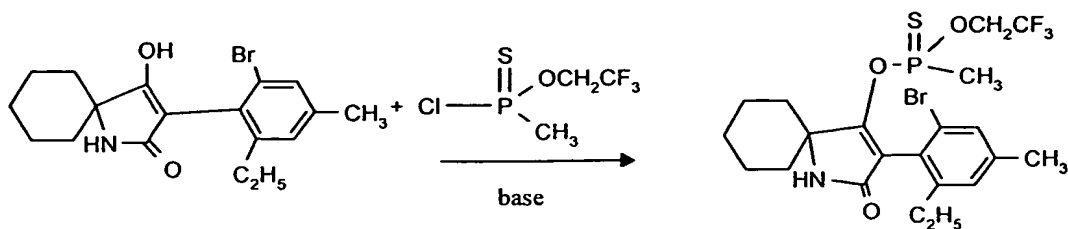


5

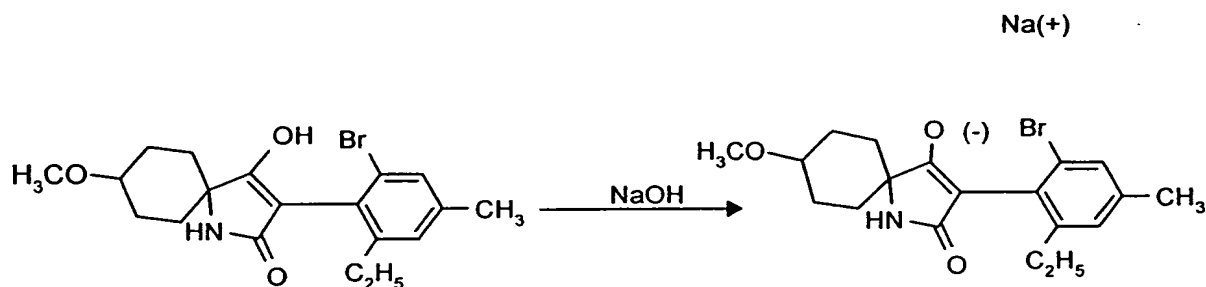
Using, for example, according to process (E) 3-[(2-bromo-4-methyl-6-ethyl)phenyl]-1-azaspiro[4,5]decane-2,4-dione and methanesulphonyl chloride as starting materials, the course of the reaction can be represented by the following reaction scheme:



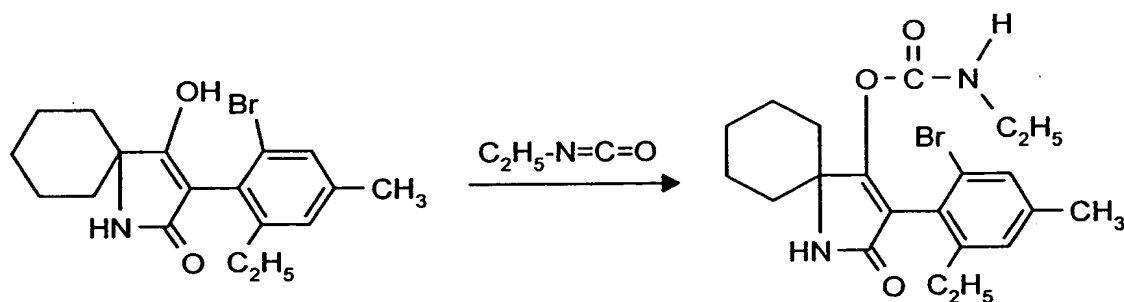
- 10 Using, for example, according to process (F) 3-[(2-bromo-4-methyl-6-ethyl)phenyl]-1-azaspiro[4,5]decane-2,4-dione and 2,2,2-trifluoroethyl methanethiophosphonyl chloride as starting materials, the course of the reaction can be represented by the following reaction scheme:



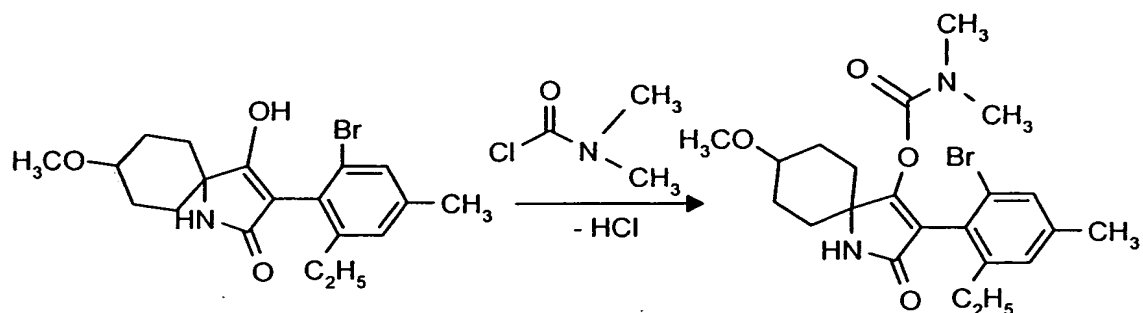
Using, for example, according to process (G) 8-methoxy-3-[(2-bromo-4-methyl-6-ethyl)phenyl]-1-azaspiro[4,5]decane-2,4-dione and NaOH as components, the course of the process according to the invention can be represented by the following reaction scheme:



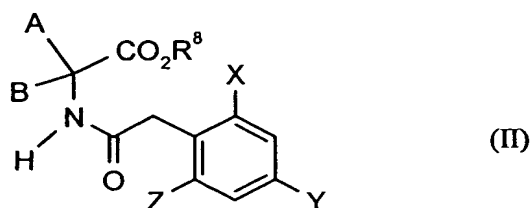
Using, for example, according to process (H), variant α , 3-[(2-bromo-4-methyl-6-ethyl)phenyl]-1-azaspiro[4,5]decane-2,4-dione and ethyl isocyanate as starting materials, the course of the reaction can be represented by the reaction scheme below:



- 10 Using, for example, according to process (H), variant β , 8-methoxy-3-[(2-bromo-4-methyl-6-ethyl)phenyl]-1-azaspiro[4,5]decane-2,4-dione and dimethylcarbamoyl chloride as starting materials, the course of the reaction may be represented by the scheme below:



The compounds, required as starting materials in the process (A) according to the invention, of the formula (II)

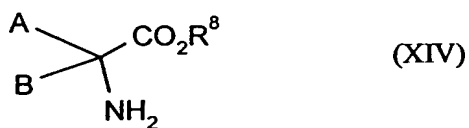


5 in which

A, B, X, Y, Z and R^8 are as defined above

are novel.

The acylamino acid esters of the formula (II) are obtained, for example, when amino acid derivatives of the formula (XIV)

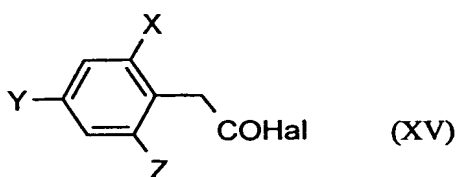


10

in which

A, B and R^8 are as defined above

are acylated with substituted phenylacetyl halides of the formula (XV)



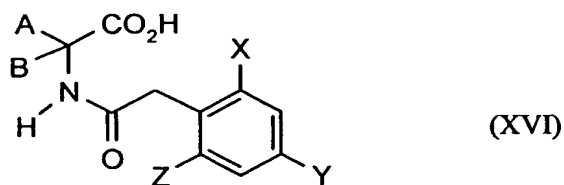
in which

X, Y and Z are as defined above and

Hal represents chlorine or bromine

(Chem. Reviews 52, 237-416 (1953); Bhattacharya, Indian J. Chem. 6, 341-5, 1968, patent literature
5 cited at the outset, for example WO 97/02243)

or when acylamino acids of the formula (XVI)

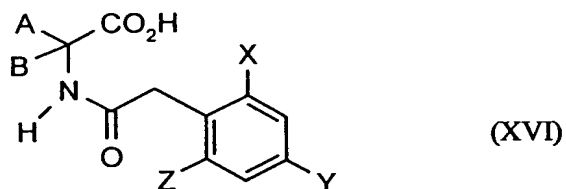


in which

A, B, X, Y and Z are as defined above

10 are esterified (Chem. Ind. (London) 1568 (1968)).

The compounds of the formula (XVI)

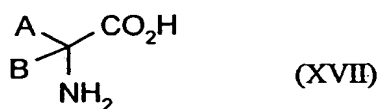


in which

A, B, X, Y and Z are as defined above

15 are likewise novel.

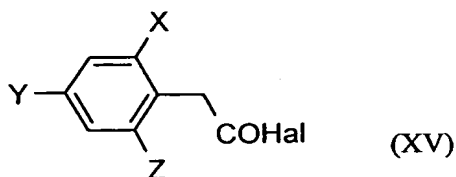
The compounds of the formula (XVI) are obtained when amino acids of the formula (XVII)



in which

A and B are as defined above

are acylated according to Schotten-Baumann with substituted phenylacetyl halides of the formula (XV)



5 in which

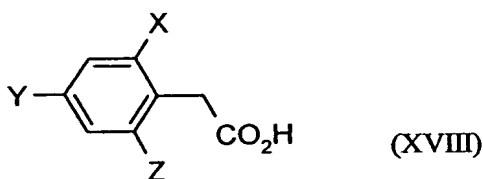
X, Y and Z are as defined above and

Hal represents chlorine or bromine

(Organikum, VEB Deutscher Verlag der Wissenschaften, Berlin 1977, p. 505).

10 Some of the compounds of the formula (XV) are novel, and they can be prepared by processes known in principle (WO 97/02243).

The compounds of the formula (XV) are obtained, for example, by reacting substituted phenylacetic acids of the formula (XVIII)



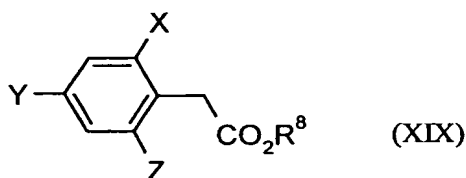
in which

15 X, Y and Z are as defined above

with halogenating agents (for example thionyl chloride, thionyl bromide, oxalyl chloride, phosgene, phosphorus trichloride, phosphorus tribromide or phosphorus pentachloride), if appropriate in the presence of a diluent (for example an optionally chlorinated aliphatic or aromatic hydrocarbon, such as toluene or methylene chloride), at temperatures of from -20°C to 150°C, preferably from -10°C to 20 100°C.

Some of the compounds of the formula (XVIII) are novel.

The compounds of the formula (XVIII) are obtained, for example, by hydrolysing substituted phenylacetic acid esters of the formula (XIX)



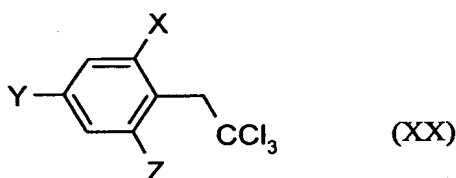
in which

- 5 X, Y, Z and R⁸ are as defined above

in the presence of an acid (for example an inorganic acid, such as hydrochloric acid) or a base (for example an alkali metal hydroxide, such as sodium hydroxide or potassium hydroxide) and, if appropriate, a diluent (for example an aqueous alcohol, such as methanol or ethanol), at temperatures between 0°C and 150°C, preferably between 20°C and 100°C.

- 10 Some of the compounds of the formula (XIX) are likewise novel, and they can be prepared by processes known in principle (WO 97/02243).

The compounds of the formula (XIX) are obtained, for example, by reacting substituted 1,1,1-trichloro-2-phenylethanes of the formula (XX),



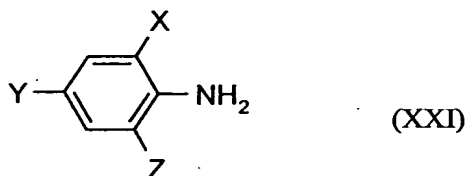
- 15 in which

X, Y and Z are as defined above,

- initially with alkoxides (for example alkali metal alkoxides, such as sodium methoxide or sodium ethoxide) in the presence of a diluent (for example the alcohol derived from the alkoxide), at temperatures between 0°C and 150°C, preferably between 20°C and 120°C, and then with an acid
- 20 (preferably an inorganic acid, such as, for example, sulphuric acid), at temperatures between -20°C and 150°C, preferably between 0°C and 100°C.

Some of the compounds of the formula (XX) are novel, and can be prepared by processes known in principle (WO 97/02243).

The compounds of the formula (XX) are obtained, for example, when anilines of the formula (XXI)



in which

X, Y and Z are as defined above

5 are reacted in the presence of an alkyl nitrite of the formula (XXII),



in which

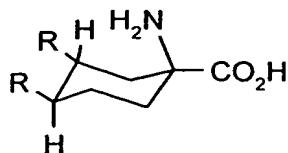
R^{13} represents alkyl, preferably $\text{C}_1\text{-C}_6\text{-alkyl}$,

10 in the presence of copper(II) chloride and, if appropriate, in the presence of a diluent (for example an aliphatic nitrile, such as acetonitrile), at a temperature of from -20°C to 80°C , preferably from 0°C to 60°C , with vinylidene chloride ($\text{CH}_2=\text{CCl}_2$).

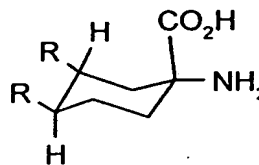
Some of the compounds of the formula (XXI) are novel, and they can be prepared by processes which are generally known in principle. The compounds of the formula (XXII) are known compounds of organic chemistry. Copper(II) chloride and vinylidene chloride have been known for a long time and
15 are commercially available.

Some of the compounds of the formulae (XIV) and (XVII) are known, and/or can be prepared by known processes (see, for example, Compagnon, Miocque Ann. Chim. (Paris) [14] 5, pp. 11-22, 23-27 (1970)).

The substituted cyclic aminocarboxylic acids of the formula (XVII) in which A and B form a ring are
20 generally obtained by means of a Bucherer-Bergs synthesis or a Strecker synthesis, where they are obtained in each case in different isomeric forms. Thus, the conditions of the Bucherer-Bergs synthesis give predominantly the isomers (for simplicity reasons referred to as β hereinbelow) in which the radicals R and the carboxyl group are in equatorial positions while the conditions of the Strecker synthesis give predominantly the isomers (for simplicity reasons referred to as α
25 hereinbelow) where the amino group and the radicals R are in equatorial positions.



Bucherer-Bergs synthesis

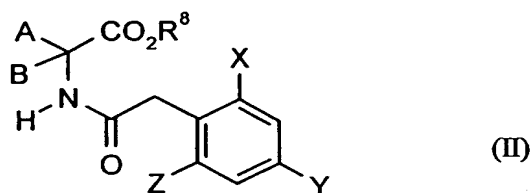
(β -isomer)

Strecker synthesis

(α -isomer)

(L. Munday, J. Chem. Soc. 4372 (1961); J.T. Eward, C. Jitrangeri, Can. J. Chem. 53, 3339 (1975).

- 5 The starting materials, used in the above process (A), of the formula (II),

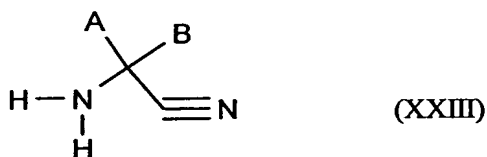


(II)

in which

A, B, X, Y, Z and R^8 are as defined above,

can furthermore be prepared by reacting aminonitriles of the formula (XXIII),



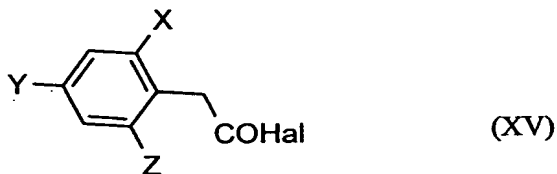
(XXIII)

10

in which

A and B are as defined above,

with substituted phenylacetyl halides of the formula (XV),

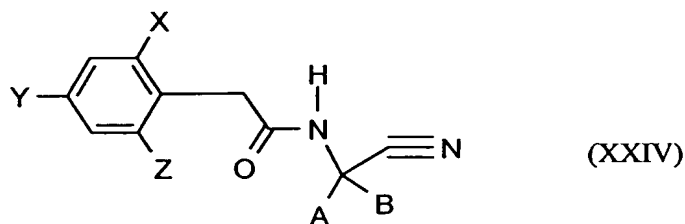


(XV)

15 in which

X, Y, Z and Hal are as defined above,

to give compounds of the formula (XXIV),



in which

5 A, B, X, Y and Z are as defined above,

and then subjecting these to an acid alcoholysis.

Some of the compounds of the formulae (XXIV) and (XXIII) are likewise novel.

10 The acid halides of the formula (III), carboxylic anhydrides of the formula (IV), chloroformic esters or chloroformic thioesters of the formula (V), chloromonothioformic esters or chlorodithioformic esters of the formula (VI), alkyl halides of the formula (VII), sulphonyl chlorides of the formula (VIII), phosphorus compounds of the formula (IX) and metal hydroxides, metal alkoxides or amines of the formulae (X) and (XI), respectively, and isocyanates of the formula (XII) and carbamoyl chlorides of the formula (XIII) furthermore required as starting materials for carrying out the processes (B), (C), (D), (E), (F), (G) and (H) according to the invention are generally known
15 compounds of organic or inorganic chemistry.

In addition, the compounds of the formulae (XIV) and (XVII) are known from the patent applications cited at the outset and/or can be prepared by the methods given therein.

20 The process (A) is characterized in that compounds of the formula (II) in which A, B, X, Y, Z and R⁸ are as defined above are subjected to an intramolecular condensation in the presence of a diluent and in the presence of a base.

Suitable diluents for the process (A) according to the invention are all organic solvents which are inert towards the reactants. Preference is given to using hydrocarbons, such as toluene and xylene, furthermore ethers, such as dibutyl ether, tetrahydrofuran, dioxane, glycol dimethyl ether and diglycol dimethyl ether, moreover polar solvents, such as dimethyl sulphoxide, sulpholane, dimethyl-
25 formamide and N-methylpyrrolidone, and also alcohols, such as methanol, ethanol, propanol, isopropanol, butanol, isobutanol and tert-butanol.

Suitable bases (deprotonating agents) for carrying out the process (A) according to the invention are all customary proton acceptors. Preference is given to using alkali metal and alkaline earth metal oxides, hydroxides and carbonates, such as sodium hydroxide, potassium hydroxide, magnesium oxide, calcium oxide, sodium carbonate, potassium carbonate and calcium carbonate, which can also be used in the presence of phase-transfer catalysts, such as, for example, triethylbenzylammonium chloride, tetrabutylammonium bromide, Adogen 464 (= methyltrialkyl(C₈-C₁₀)ammonium chloride) or TDA 1 (= tris(methoxyethoxyethyl)amine). It is furthermore possible to use alkali metals, such as sodium or potassium. Also suitable are alkali metal and alkaline earth metal amides and hydrides, such as sodium amide, sodium hydride and calcium hydride, and additionally also alkali metal alkoxides, such as sodium methoxide, sodium ethoxide and potassium tert-butoxide.

When carrying out the process (A) according to the invention, the reaction temperature can be varied within a relatively wide range. In general, the process is carried out at temperatures between 0°C and 250°C, preferably between 50°C and 150°C.

The process (A) according to the invention is generally carried out under atmospheric pressure.

When carrying out the process (A) according to the invention, the reaction component of the formula (II) and the deprotonating base are generally employed in equimolar to about doubly equimolar amounts. However, it is also possible to use a relatively large excess (up to 3 mol) of one component or the other.

The process (B α) is characterized in that compounds of the formula (I-a) are in each case reacted with carbonyl halides of the formula (III), if appropriate in the presence of a diluent and if appropriate in the presence of an acid binder.

Suitable diluents for the process (B α) according to the invention are all solvents which are inert towards the acid halides. Preference is given to using hydrocarbons, such as benzene, toluene, xylene and tetralin, furthermore halogenated hydrocarbons, such as methylene chloride, chloroform, carbon tetrachloride, chlorobenzene and o-dichlorobenzene, moreover ketones, such as acetone and methyl isopropyl ketone, furthermore ethers, such as diethyl ether, tetrahydrofuran and dioxane, additionally carboxylic esters, such as ethyl acetate, and also strongly polar solvents, such as dimethyl sulphoxide and sulpholane. The hydrolytic stability of the acid halide permitting, the reaction can also be carried out in the presence of water.

Suitable acid binders for the reaction according to process (B α) according to the invention are all customary acid acceptors. Preference is given to using tertiary amines, such as triethylamine, pyridine, diazabicyclooctane (DABCO), diazabicycloundecene (DBU), diazabicyclononene (DBN),

Hünig base and N,N-dimethylaniline, furthermore alkaline earth metal oxides, such as magnesium oxide and calcium oxide, moreover alkali metal and alkaline earth metal carbonates, such as sodium carbonate, potassium carbonate and calcium carbonate, and also alkali metal hydroxides, such as sodium hydroxide and potassium hydroxide.

- 5 In the process (B α) according to the invention, the reaction temperature can be varied within a relatively wide range. In general, the process is carried out at temperatures between -20°C and +150°C, preferably between 0°C and 100°C.

When carrying out the process (B α) according to the invention, the starting materials of the formula (I-a) and the carbonyl halide of the formula (III) are generally each employed in approximately
10 equivalent amounts. However, it is also possible to use a relatively large excess (up to 5 mol) of the carbonyl halide. Work-up is carried out by customary methods.

The process (B β) is characterized in that compounds of the formula (I-a) are in each case reacted with carboxylic anhydrides of the formula (IV), if appropriate in the presence of a diluent and if appropriate in the presence of an acid binder.

- 15 Suitable diluents for the process (B β) according to the invention are preferably those diluents which are also preferred when using acid halides. Furthermore, excess carboxylic anhydride may simultaneously act as diluent.

The acid binders which are added, if appropriate, in the process (B β) are preferably those acid binders which are also preferred when using acid halides.

- 20 The reaction temperature in the process (B β) according to the invention may be varied within a relatively wide range. In general, the process is carried out at temperatures between -20°C and +150°C, preferably between 0°C and 100°C.

When carrying out the process (B β) according to the invention, the starting materials of the formula (I-a) and the carboxylic anhydride of the formula (IV) are generally each employed in approximately
25 equivalent amounts. However, it is also possible to use a relatively large excess (up to 5 mol) of the carboxylic anhydride. Work-up is carried out by customary methods.

In general, diluent and excess carboxylic anhydride and the carboxylic acid formed are removed by distillation or by washing with an organic solvent or with water.

The process (C) is characterized in that compounds of the formula (I-a) are in each case reacted with chloroformic esters or chloroformic thioesters of the formula (V) if appropriate in the presence of a diluent and if appropriate in the presence of an acid binder.

Suitable acid binders for the process (C) according to the invention are all customary acid acceptors.

- 5 Preference is given to using tertiary amines, such as triethylamine, pyridine, DABCO, DBU, DBA, Hünig base and N,N-dimethylaniline, furthermore alkaline earth metal oxides, such as magnesium oxide and calcium oxide, moreover alkali metal and alkaline earth metal carbonates, such as sodium carbonate, potassium carbonate and calcium carbonate, and also alkali metal hydroxides, such as sodium hydroxide and potassium hydroxide.

- 10 Suitable diluents for the process (C) according to the invention are all solvents which are inert towards the chloroformic esters or chloroformic thioesters. Preference is given to using hydrocarbons, such as benzene, toluene, xylene and tetralin, furthermore halogenated hydrocarbons, such as methylene chloride, chloroform, carbon tetrachloride, chlorobenzene and o-dichlorobenzene, moreover ketones, such as acetone and methyl isopropyl ketone, furthermore ethers, such as diethyl
15 ether, tetrahydrofuran and dioxane, additionally carboxylic esters, such as ethyl acetate, and also strongly polar solvents, such as dimethyl sulphoxide and sulfolane.

When carrying out the process (C) according to the invention, the reaction temperature can be varied within a relatively wide range. In general, the reaction temperature is between -20°C and +100°C, preferably between 0°C and 50°C.

- 20 The process (C) according to the invention is generally carried out under atmospheric pressure.

- When carrying out the process (C) according to the invention, the starting materials of the formula (I-a) and the appropriate chloroformic ester or chloroformic thioester of the formula (V) are generally each employed in approximately equivalent amounts. However, it is also possible to use a relatively large excess (up to 2 mol) of one component or the other. Work-up is carried out by customary
25 methods. In general, precipitated salts are removed and the reaction mixture which remains is concentrated by removing the diluent under reduced pressure.

- The process (D) according to the invention is characterized in that compounds of the formula (I-a) are in each case reacted with (D α) compounds of the formula (VI) in the presence of a diluent and, if appropriate, in the presence of an acid binder or (D β) carbon disulphide and then with alkyl halides of
30 the formula (VII), if appropriate in the presence of a diluent and if appropriate in the presence of a base.

In preparation process (D α), about 1 mol of chloromonothioformic ester or chlorodithioformic ester of the formula (VI) is reacted per mole of starting material of the formula (I-a), at from 0 to 120°C, preferably from 20 to 60°C.

Suitable diluents, which are added, if appropriate, are all inert polar organic solvents, such as ethers, esters, amides, sulphones, sulphoxides, but also halogenated alkanes.

Preference is given to using dimethyl sulphoxide, ethyl acetate, tetrahydrofuran, dimethylformamide or methylene chloride.

If, in a preferred embodiment, the enolate salt of the compound (I-a) is prepared by adding strong deprotonating agents, such as, for example, sodium hydride or potassium tert-butoxide, the further addition of acid binders may be dispensed with.

If acid binders are used, these are customary inorganic or organic bases, for example sodium hydroxide, sodium carbonate, potassium carbonate, pyridine and triethylamine.

The reaction can be carried out at atmospheric pressure or under elevated pressure and is preferably carried out at atmospheric pressure. Work-up is carried out by customary methods.

In preparation process (D β), in each case the equimolar amount or an excess of carbon disulphide is added per mole of starting material of the formula (I-a). The process is preferably carried out at temperatures of from 0 to 50°C and in particular at from 20 to 30°C.

Frequently, it is expedient to prepare initially the corresponding salt from the compounds of the formula (I-a) by adding a base (such as, for example, potassium tert-butoxide or sodium hydride). In each case, the compound (I-a) is reacted with carbon disulphide until the formation of the intermediate has ended, for example after several hours of stirring at room temperature.

Suitable bases for process (D β) are all customary proton acceptors. Preference is given to using alkali metal hydrides, alkali metal alkoxides, alkali metal and alkaline earth metal carbonates or bicarbonates or nitrogen bases. Examples which may be mentioned are sodium hydride, sodium methoxide, sodium hydroxide, calcium hydroxide, potassium carbonate, sodium bicarbonate, triethylamine, dibenzylamine, diisopropylethylamine, pyridine, quinoline, diazabicyclooctane (DABCO), diazabicyclononene (DBN) and diazabicycloundecene (DBU).

Suitable diluents are all solvents which are customary for this process.

Preference is given to using aromatic hydrocarbons, such as benzene or toluene, alcohols, such as methanol, ethanol, isopropanol or ethylene glycol, nitriles, such as acetonitrile, ethers, such as

tetrahydrofuran or dioxane, amides, such as dimethylformamide, or other polar solvents, such as dimethyl sulphoxide or sulfolane.

The further reaction with the alkyl halide of the formula (VII) is preferably carried out at from 0 to 70°C and in particular at from 20 to 50°C. Here, at least an equimolar amount of alkyl halide is used.

- 5 The process is carried out at atmospheric pressure or under elevated pressure, preferably at atmospheric pressure.

Work-up is again carried out by customary methods.

- 10 The process (E) according to the invention is characterized in that compounds of the formula (I-a) are in each case reacted with sulphonyl chlorides of the formula (VIII), if appropriate in the presence of a diluent and if appropriate in the presence of an acid binder.

In the preparation process (E), about 1 mol of sulphonyl chloride of the formula (VIII) is reacted per mole of starting material of the formula (I-a), at from -20 to 150°C, preferably from 20 to 70°C.

The process (E) is preferably carried out in the presence of a diluent.

- 15 Suitable diluents are all inert polar organic solvents, such as ethers, esters, amides, nitriles, sulphones, sulphoxides or halogenated hydrocarbons, such as methylene chloride.

Preference is given to using dimethyl sulphoxide, tetrahydrofuran, ethyl acetate, dimethylformamide, methylene chloride.

- 20 If, in a preferred embodiment, the enolate salt of the compound (I-a) is prepared by adding strong deprotonating agents (such as, for example, sodium hydride or potassium tert-butoxide), the further addition of acid binders may be dispensed with.

If acid binders are used, these are customary inorganic or organic bases, for example sodium hydroxide, sodium carbonate, potassium carbonate, pyridine and triethylamine.

The reaction can be carried out at atmospheric pressure or under elevated pressure and is preferably carried out at atmospheric pressure. Work-up is carried out by customary methods.

- 25 The process (F) according to the invention is characterized in that compounds of the formula (I-a) are in each case reacted with phosphorus compounds of the formula (IX), if appropriate in the presence of a diluent and if appropriate in the presence of an acid binder.

In preparation process (F), to obtain compounds of the formula (I-e), 1 to 2, preferably 1 to 1.3, mol of the phosphorus compound of the formula (IX) are reacted per mole of the compound (I-a), at temperatures between -40°C and 150°C, preferably between -10 and 110°C.

The process (F) is preferably carried out in the presence of a diluent.

- 5 Suitable diluents are all inert polar organic solvents, such as ethers, esters, amides, nitriles, sulphides, sulphones, sulphoxides, etc.

Preference is given to using acetonitrile, ethyl acetate, dimethyl sulphoxide, tetrahydrofuran, dimethylformamide, methylene chloride.

- 10 Suitable acid binders, which are added, if appropriate, are customary inorganic or organic bases, such as hydroxides, carbonates or amines. Examples which may be mentioned are sodium hydroxide, sodium carbonate, potassium carbonate, pyridine and triethylamine.

- 15 The reaction can be carried out at atmospheric pressure or under elevated pressure and is preferably carried out at atmospheric pressure. Work-up is carried out by customary methods of organic chemistry. The end products are preferably purified by crystallization, chromatographic purification or by "incipient distillation", i.e. removal of the volatile components under reduced pressure.

The process (G) is characterized in that compounds of the formula (I-a) are in each case reacted with metal hydroxides or metal alkoxides of the formula (X) or amines of the formula (XI), if appropriate in the presence of a diluent.

- 20 Suitable diluents for the process (G) according to the invention are preferably ethers, such as tetrahydrofuran, dioxane, diethyl ether or else alcohols, such as methanol, ethanol, isopropanol, but also water. The process (G) according to the invention is generally carried out under atmospheric pressure. The reaction temperature is generally between -20°C and 100°C, preferably between 0°C and 50°C.

- 25 The process (H) according to the invention is characterized in that compounds of the formula (I-a) are in each case reacted with (H α) compounds of the formula (XII), if appropriate in the presence of a diluent and if appropriate in the presence of a catalyst, or (H β) with compounds of the formula (XIII), if appropriate in the presence of a diluent and if appropriate in the presence of an acid binder.

In preparation process (H α), about 1 mol of isocyanate of the formula (XII) is reacted per mole of starting material of the formula (I-a), at from 0 to 100°C, preferably at from 20 to 50°C.

- 30 The process (H α) is preferably carried out in the presence of a diluent.

Suitable diluents are all inert organic solvents, such as ethers, esters, amides, nitriles, sulphones or sulphoxides.

If appropriate, catalysts may be added to accelerate the reaction. Suitable for use as catalysts are, very advantageously, organotin compounds, such as, dibutyltin dilaurate.

- 5 The process is preferably carried out at atmospheric pressure.

In the preparation process (H β), about 1 mol of carbamoyl chloride of the formula (XIII) is reacted per mole of starting material of the formula (I-a), at from 0 to 150°C, preferably at from 20 to 70°C.

Suitable diluents which are added, if appropriate, are all inert polar organic solvents, such as ethers, esters, amides, sulphones, sulphoxides or halogenated hydrocarbons.

- 10 Preference is given to using dimethyl sulphoxide, ethyl acetate, tetrahydrofuran, dimethylformamide or methylene chloride.

If, in a preferred embodiment, the enolate salt of the compound (I-a) is prepared by adding strong deprotonating agents (such as, for example, sodium hydride or potassium tert-butoxide), the further addition of acid binders may be dispensed with.

- 15 If acid binders are used, these are customary inorganic or organic bases, for example sodium hydroxide, sodium carbonate, potassium carbonate, triethylamine or pyridine.

The reaction can be carried out at atmospheric pressure or under elevated pressure and is preferably carried out at atmospheric pressure. Work-up is carried out by customary methods.

- 20 The active compounds are well tolerated by plants and have advantageous toxicity to warm-blooded species; they can be employed for controlling animal pests, in particular insects, arachnids and nematodes encountered in agriculture, forests, in the protection of stored products and materials and in the hygiene sector. They are preferably used as crop protection agents. They are active against normally sensitive and resistant species and against all or some stages of development. The abovementioned pests include:

- 25 From the order of the Isopoda, for example, *Oniscus asellus*, *Armadillidium vulgare* and *Porcellio scaber*.

From the order of the Diplopoda, for example, *Blaniulus guttulatus*.

From the order of the Chilopoda, for example, *Geophilus carpophagus* and *Scutigera* spp.

From the order of the Symphyla, for example, *Scutigera immaculata*.

From the order of the Thysanura, for example, *Lepisma saccharina*.

From the order of the Collembola, for example, *Onychiurus armatus*.

From the order of the Orthoptera, for example, *Acheta domesticus*, *Gryllotalpa* spp., *Locusta*
5 *migratoria migratorioides*, *Melanoplus* spp. and *Schistocerca gregaria*.

From the order of the Blattaria, for example, *Blatta orientalis*, *Periplaneta americana*, *Leucophaea maderae* and *Blattella germanica*.

From the order of the Dermaptera, for example, *Forficula auricularia*.

From the order of the Isoptera, for example, *Reticulitermes* spp.

10 From the order of the Phthiraptera, for example, *Pediculus humanus corporis*, *Haematopinus* spp., *Linognathus* spp., *Trichodectes* spp., *Damalinia* spp.

From the order of the Thysanoptera, for example, *Hercinothrips femoralis*, *Thrips tabaci*, *Thrips palmi*, *Frankliniella occidentalis*.

From the order of the Heteroptera, for example, *Eurygaster* spp., *Dysdercus intermedius*, *Piesma*
15 *quadrata*, *Cimex lectularius*, *Rhodnius prolixus* and *Triatoma* spp.

From the order of the Homoptera, for example, *Aleurodes brassicae*, *Bemisia tabaci*, *Trialeurodes vaporariorum*, *Aphis gossypii*, *Brevicoryne brassicae*, *Cryptomyzus ribis*, *Aphis fabae*, *Aphis pomi*, *Eriosoma lanigerum*, *Hyalopterus arundinis*, *Phylloxera vastatrix*, *Pemphigus* spp., *Macrosiphum avenae*, *Myzus* spp., *Phorodon humuli*, *Rhopalosiphum padi*, *Empoasca* spp., *Euscelis bilobatus*,
20 *Nephotettix cincticeps*, *Lecanium corni*, *Saissetia oleae*, *Laodelphax striatellus*, *Nilaparvata lugens*, *Aonidiella aurantii*, *Aspidiotus hederae*, *Pseudococcus* spp. and *Psylla* spp.

From the order of the Lepidoptera, for example, *Pectinophora gossypiella*, *Bupalus piniarius*, *Cheimatobia brumata*, *Lithocolletis blancardella*, *Hyponomeuta padella*, *Plutella xylostella*, *Malacosoma neustria*, *Euproctis chrysorrhoea*, *Lymantria* spp., *Bucculatrix thurberiella*, *Phyllocnistis*
25 *citrella*, *Agrotis* spp., *Euxoa* spp., *Feltia* spp., *Earias insulana*, *Heliothis* spp., *Mamestra brassicae*, *Panolis flammea*, *Spodoptera* spp., *Trichoplusia ni*, *Carpocapsa pomonella*, *Pieris* spp., *Chilo* spp., *Pyrausta nubilalis*, *Ephestia kuehniella*, *Galleria mellonella*, *Tineola bisselliella*, *Tinea pellionella*, *Hofmannophila pseudospretella*, *Cacoecia podana*, *Capua reticulana*, *Choristoneura fumiferana*, *Clysia ambiguella*, *Homona magnanima*, *Tortrix viridana*, *Cnaphalocerus* spp. and *Oulema oryzae*.

- From the order of the Coleoptera, for example, *Anobium punctatum*, *Rhizopertha dominica*, *Bruchidius obtectus*, *Acanthoscelides obtectus*, *Hylotrupes bajulus*, *Agelastica alni*, *Leptinotarsa decemlineata*, *Phaedon cochleariae*, *Diabrotica* spp., *Psylliodes chrysocephala*, *Epilachna varivestis*, *Atomaria* spp., *Oryzaephilus surinamensis*, *Anthonomus* spp., *Sitophilus* spp., *Otiorrhynchus* 5 *sulcatus*, *Cosmopolites sordidus*, *Ceuthorrhynchus assimilis*, *Hypera postica*, *Dermestes* spp., *Trogoderma* spp., *Anthrenus* spp., *Attagenus* spp., *Lyctus* spp., *Meligethes aeneus*, *Ptinus* spp., *Niptus hololeucus*, *Gibbium psylloides*, *Tribolium* spp., *Tenebrio molitor*, *Agriotes* spp., *Conoderus* spp., *Melolontha melolontha*, *Amphimallon solstitialis*, *Costelytra zealandica* and *Lissorhoptus oryzophilus*.
- 10 From the order of the Hymenoptera, for example, *Diprion* spp., *Hoplocampa* spp., *Lasius* spp., *Monomorium pharaonis* and *Vespa* spp.

- From the order of the Diptera, for example, *Aedes* spp., *Anopheles* spp., *Culex* spp., *Drosophila melanogaster*, *Musca* spp., *Fannia* spp., *Calliphora erythrocephala*, *Lucilia* spp., *Chrysomya* spp., *Cuterebra* spp., *Gastrophilus* spp., *Hyppobosca* spp., *Stomoxys* spp., *Oestrus* spp., *Hypoderma* spp., 15 *Tabanus* spp., *Tannia* spp., *Bibio hortulanus*, *Oscinella frit*, *Phorbia* spp., *Pegomyia hyoscyami*, *Ceratitis capitata*, *Dacus oleae*, *Tipula paludosa*, *Hylemyia* spp. and *Liriomyza* spp.

From the order of the Siphonaptera, for example, *Xenopsylla cheopis* and *Ceratophyllus* spp.

- From the class of the Arachnida, for example, *Scorpio maurus*, *Latrodectus mactans*, *Acarus siro*, *Argas* spp., *Ornithodoros* spp., *Dermanyssus gallinae*, *Eriophyes ribis*, *Phyllocoptruta oleivora*, 20 *Boophilus* spp., *Rhipicephalus* spp., *Amblyomma* spp., *Hyalomma* spp., *Ixodes* spp., *Psoroptes* spp., *Chorioptes* spp., *Sarcoptes* spp., *Tarsonemus* spp., *Bryobia praetiosa*, *Panonychus* spp., *Tetranychus* spp., *Hemitarsonemus* spp. and *Brevipalpus* spp.

- The plant-parasitic nematodes include, for example, *Pratylenchus* spp., *Radopholus similis*, *Ditylenchus dipsaci*, *Tylenchulus semipenetrans*, *Heterodera* spp., *Globodera* spp., *Meloidogyne* 25 spp., *Aphelenchoides* spp., *Longidorus* spp., *Xiphinema* spp., *Trichodorus* spp. and *Bursaphelenchus* spp.

If appropriate, the compounds or active compound combinations according to the invention may also be used in certain concentrations or application rates to act as herbicides. If appropriate, they can also be employed as intermediates or precursors for the synthesis of further active compounds.

- 30 All plants and plant parts can be treated in accordance with the invention. Plants are to be understood as meaning in the present context all plants and plant populations such as desired and undesired wild plants or crop plants (including naturally occurring crop plants). Crop plants can be

plants which can be obtained by conventional plant breeding and optimization methods or by biotechnological and recombinant methods or by combinations of these methods, including the transgenic plants and inclusive of the plant cultivars protectable or not protectable by plant breeders' rights. Plant parts are to be understood as meaning all parts and organs of plants above and below the ground, such as shoot, leaf, flower and root, examples which may be mentioned being leaves, needles, stalks, stems, flowers, fruit bodies, fruits, seeds, roots, tubers and rhizomes. The plant parts also include harvested material, and vegetative and generative propagation material, for example cuttings, tubers, rhizomes, offsets and seeds.

The treatment according to the invention of the plants and plant parts with the active compounds or active compound combinations is carried out directly or by allowing the compounds to act on their surroundings, habitat or storage space by the customary treatment methods, for example by immersion, spraying, evaporation, fogging, scattering or painting on and, in the case of propagation material, in particular in the case of seeds, also by applying one or more coats.

The active compounds or active compound combinations can be converted into the customary formulations such as solutions, emulsions, wettable powders, suspensions, powders, dusts, pastes, soluble powders, granules, suspension-emulsion concentrates, natural and synthetic materials impregnated with active compound, and microencapsulations in polymeric materials.

These formulations are produced in a known manner, for example by mixing the active compounds with extenders, that is, liquid solvents and/or solid carriers, optionally with the use of surfactants, that is, emulsifiers and/or dispersants, and/or foam formers.

If the extender used is water, it is also possible, for example, to use organic solvents as cosolvents. The following are essentially suitable as liquid solvents: aromatics such as xylene, toluene or alkylnaphthalenes, chlorinated aromatics or chlorinated aliphatic hydrocarbons such as chlorobenzenes, chloroethylenes or methylene chloride, aliphatic hydrocarbons such as cyclohexane or paraffins, for example mineral oil fractions, mineral and vegetable oils, alcohols such as butanol or glycol and their ethers and esters, ketones such as acetone, methyl ethyl ketone, methyl isobutyl ketone or cyclohexanone, strongly polar solvents such as dimethylformamide and dimethyl sulphoxide, or else water.

Suitable solid carriers are:

for example ammonium salts and ground natural minerals such as kaolins, clays, talc, chalk, quartz, attapulgite, montmorillonite or diatomaceous earth, and ground synthetic materials such as highly-disperse silica, alumina and silicates; suitable solid carriers for granules are: for example

crushed and fractionated natural rocks such as calcite, marble, pumice, sepiolite and dolomite, or else synthetic granules of inorganic and organic meals, and granules of organic material such as sawdust, coconut shells, maize cobs and tobacco stalks; suitable emulsifiers and/or foam formers are: for example nonionic and anionic emulsifiers such as polyoxyethylene fatty acid esters, polyoxyethylene fatty alcohol ethers, for example alkylaryl polyglycol ethers, alkylsulphonates, alkyl sulphates, arylsulphonates, or else protein hydrolysates; suitable dispersants are: for example lignin-sulphite waste liquors and methylcellulose.

Tackifiers such as carboxymethylcellulose and natural and synthetic polymers in the form of powders, granules or latices, such as gum arabic, polyvinyl alcohol and polyvinyl acetate, or else natural phospholipids such as cephalins and lecithins and synthetic phospholipids can be used in the formulations. Other additives can be mineral and vegetable oils.

It is possible to use colorants such as inorganic pigments, for example iron oxide, titanium oxide and Prussian Blue, and organic colorants such as alizarin colorants, azo colorants and metal phthalocyanine colorants, and trace nutrients such as salts of iron, manganese, boron, copper, cobalt, molybdenum and zinc.

The formulations generally comprise between 0.1 and 95% by weight of active compound, preferably between 0.5 and 90%.

The active compounds according to the invention, as such or in their formulations, can also be used as a mixture with known fungicides, bactericides, acaricides, nematocides or insecticides, for example in order to widen the spectrum of action or to prevent the development of resistances in this way. In many cases, synergistic effects result, i.e. the activity of the mixture exceeds the activity of the individual components.

Compounds which are suitable as components in the mixtures are, for example, the following:

Fungicides:

aldimorph, ampropylfos, ampropylfos-potassium, andoprim, anilazine, azaconazole, azoxystrobin, benalaxyl, benodanil, benomyl, benzamacril, benzamacril-isobutyl, bialaphos, binapacryl, biphenyl, bitertanol, blasticidin-S, bromuconazole, bupirimate, buthiobate, calcium polysulphide, capsimycin, captafol, captan, carbendazim, carboxin, carvon, quinomethionate, chlobenthiazole, chlorfenazole, chloroneb, chloropicrin, chlorothalonil, chlozolate, clozylacon, cufraneb, cymoxanil, cyproconazole, cyprodinil, cyprofuram,

- debacarb, dichlorophen, diclobutrazole, diclofluanid, diclomezine, dicloran, diethofencarb, difenoconazole, dimethirimol, dimethomorph, diniconazole, diniconazole-M, dinocap, diphenylamine, dipyrithione, ditalimfos, dithianon, dodemorph, dodine, drazoxolon,
- edifenphos, epoxiconazole, etaconazole, ethirimol, etridiazole,
- 5 famoxadon, fenapanil, fenarimol, fenbuconazole, fenfuram, fenitropan, fenpiclonil, fenpropidin, fenpropimorph, fentin acetate, fentin hydroxide, ferbam, ferimzone, fluazinam, flumetover, fluoromide, fluquinconazole, flurprimidol, flusilazole, flusulfamide, flutolanil, flutriafol, folpet, fosetyl-aluminium, fosetyl-sodium, fthalide, fuberidazole, furalaxyl, furametpyr, furcarbonil, furconazole, furconazole-cis, furmecyclox,
- 10 guazatine,
- hexachlorobenzene, hexaconazole, hymexazole,
- imazalil, imibenconazole, iminoctadine, iminoctadine albesilate, iminoctadine triacetate, iodocarb, ipconazole, iprobenfos (IBP), iprodione, irumamycin, isoprothiolane, isovaledione,
- kasugamycin, kresoxim-methyl, copper preparations, such as: copper hydroxide, copper
- 15 naphthenate, copper oxychloride, copper sulphate, copper oxide, oxine-copper and Bordeaux mixture,
- mancopper, mancozeb, maneb, meferimzone, mepanipyrim, mepronil, metalaxyl, metconazole, methasulfocarb, methfuroxam, metiram, metomeclam, metsulfovax, mildiomyacin, myclobutanil, myclozolin,
- 20 nickel dimethyldithiocarbamate, nitrothal-isopropyl, nuarimol,
- ofurace, oxadixyl, oxamocarb, oxolinic acid, oxycarboxim, oxyfenthiiin,
- paclobutrazole, pefurazoate, penconazole, pencycuron, phosdiphen, picoxystrobin, pimaricin, piperalin, polyoxin, polyoxorim, probenazole, prochloraz, procymidone, propamocarb, propanosine-sodium, propiconazole, propineb, pyraclostrobin, pyrazophos, pyrifenox,
- 25 pyrimethanil, pyroquilon, pyroxyfur,
- quinconazole, quintozone (PCNB),
- sulphur and sulphur preparations,

tebuconazole, tecloftalam, tecnazene, tetcyclacis, tetraconazole, thiabendazole, thicyofen, thifluzamide, thiophanate-methyl, thiram, tioxyimide, tolclofos-methyl, tolylfluanid, triadimefon, triadimenol, triazbutil, triazoxide, trichlamide, tricyclazole, tridemorph, trifloxystrobin, triflumizole, triforine, triticonazole,

5 uniconazole,

validamycin A, vinclozolin, viniconazole,

zarilamide, zineb, ziram and also

Dagger G,

OK-8705,

10 OK-8801,

α -(1,1-dimethylethyl)- β -(2-phenoxyethyl)-1H-1,2,4-triazole-1-ethanol,

α -(2,4-dichlorophenyl)- β -fluoro- β -propyl-1H-1,2,4-triazole-1-ethanol,

α -(2,4-dichlorophenyl)- β -methoxy- α -methyl-1H-1,2,4-triazole-1-ethanol,

15 α -(5-methyl-1,3-dioxan-5-yl)- β -[[4-(trifluoromethyl)phenyl]methylene]-1H-1,2,4-triazole-1-ethanol,

(5RS,6RS)-6-hydroxy-2,2,7,7-tetramethyl-5-(1H-1,2,4-triazol-1-yl)-3-octanone,

(E)- α -(methoxyimino)-N-methyl-2-phenoxyphenylacetamide,

1-isopropyl{2-methyl-1-[[[1-(4-methylphenyl)ethyl]amino]carbonyl]propyl}carbamate,

1-(2,4-dichlorophenyl)-2-(1H-1,2,4-triazol-1-yl)ethanone O-(phenylmethyl)oxime,

20 1-(2-methyl-1-naphthalenyl)-1H-pyrrole-2,5-dione,

1-(3,5-dichlorophenyl)-3-(2-propenyl)-2,5-pyrrolidinedione,

1-[(diiodomethyl)sulphonyl]-4-methylbenzene,

1-[[2-(2,4-dichlorophenyl)-1,3-dioxolan-2-yl]methyl]-1H-imidazole,

1-[[2-(4-chlorophenyl)-3-phenyloxiranyl]methyl]-1H-1,2,4-triazole,

- 1-[1-[2-[(2,4-dichlorophenyl)methoxy]phenyl]ethenyl]-1H-imidazole,
- 1-methyl-5-nonyl-2-(phenylmethyl)-3-pyrrolidinol,
- 2',6'-dibromo-2-methyl-4'-trifluoromethoxy-4'-trifluoromethyl-1,3-thiazole-5-carboxanilide,
- 2,2-dichloro-N-[1-(4-chlorophenyl)ethyl]-1-ethyl-3-methylcyclopropanecarboxamide,
- 5 2,6-dichloro-5-(methylthio)-4-pyrimidinyl thiocyanate,
- 2,6-dichloro-N-(4-trifluoromethylbenzyl)benzamide,
- 2,6-dichloro-N-[[4-(trifluoromethyl)phenyl]methyl]benzamide,
- 2-(2,3,3-triiodo-2-propenyl)-2H-tetrazole,
- 2-[(1-methylethyl)sulphonyl]-5-(trichloromethyl)-1,3,4-thiadiazole,
- 10 2-[[6-deoxy-4-O-(4-O-methyl-β-D-glycopyranosyl)-α-D-glucopyranosyl]amino]-4-methoxy-1H-pyrrolo[2,3-d]pyrimidine-5-carbonitrile,
- 2-aminobutane,
- 2-bromo-2-(bromomethyl)pentanedinitrile,
- 2-chloro-N-(2,3-dihydro-1,1,3-trimethyl-1H-inden-4-yl)-3-pyridinecarboxamide,
- 15 2-chloro-N-(2,6-dimethylphenyl)-N-(isothiocyanatomethyl)acetamide,
- 2-phenylphenol (OPP),
- 3,4-dichloro-1-[4-(difluoromethoxy)phenyl]-1H-pyrrole-2,5-dione,
- 3,5-dichloro-N-[cyano-[(1-methyl-2-propynyl)oxy]methyl]benzamide,
- 3-(1,1-dimethylpropyl)-1-oxo-1H-indene-2-carbonitrile,
- 20 3-[2-(4-chlorophenyl)-5-ethoxy-3-isoxazolidinyl]pyridine,
- 4-chloro-2-cyano-N,N-dimethyl-5-(4-methylphenyl)-1H-imidazole-1-sulphonamide,
- 4-methyltetrazolo[1,5-a]quinazolin-5(4H)-one,
- 8-(1,1-dimethylethyl)-N-ethyl-N-propyl-1,4-dioxaspiro[4.5]decane-2-methanamine,

- 8-hydroxyquinoline sulphate,
- 9H-xanthene-2-[(phenylamino)carbonyl]-9-carboxylic hydrazide,
- bis-(1-methylethyl)-3-methyl-4-[(3-methylbenzoyl)oxy]-2,5-thiophene dicarboxylate,
- cis-1-(4-chlorophenyl)-2-(1H-1,2,4-triazol-1-yl)cycloheptanol,
- 5 cis-4-[3-[4-(1,1-dimethylpropyl)phenyl-2-methylpropyl]-2,6-dimethylmorpholine hydrochloride,
- ethyl [(4-chlorophenyl)azo]cyanoacetate,
- potassium bicarbonate,
- methanetetraethiol sodium salt,
- methyl 1-(2,3-dihydro-2,2-dimethyl-1H-inden-1-yl)-1H-imidazole-5-carboxylate,
- 10 methyl N-(2,6-dimethylphenyl)-N-(5-isoxazolylcarbonyl)-DL-alaninate,
- methyl N-(chloroacetyl)-N-(2,6-dimethylphenyl)-DL-alaninate,
- N-(2,3-dichloro-4-hydroxyphenyl)-1-methylcyclohexanecarboxamide,
- N-(2,6-dimethylphenyl)-2-methoxy-N-(tetrahydro-2-oxo-3-furanyl)acetamide,
- N-(2,6-dimethylphenyl)-2-methoxy-N-(tetrahydro-2-oxo-3-thienyl)acetamide,
- 15 N-(2-chloro-4-nitrophenyl)-4-methyl-3-nitrobenzenesulphonamide,
- N-(4-cyclohexylphenyl)-1,4,5,6-tetrahydro-2-pyrimidinamine,
- N-(4-hexylphenyl)-1,4,5,6-tetrahydro-2-pyrimidinamine,
- N-(5-chloro-2-methylphenyl)-2-methoxy-N-(2-oxo-3-oxazolidinyl)acetamide,
- N-(6-methoxy)-3-pyridinylcyclopropanecarboxamide,
- 20 N-[2,2,2-trichloro-1-[(chloroacetyl)amino]ethyl]benzamide,
- N-[3-chloro-4,5-bis(2-propinyloxy)phenyl]-N'-methoxymethanimidamide,
- N-formyl-N-hydroxy-DL-alanine sodium salt,
- O,O-diethyl [2-(dipropylamino)-2-oxoethyl]ethylphosphoramidothioate,

O-methyl S-phenyl phenylpropylphosphoramidothioate,

S-methyl 1,2,3-benzothiadiazole-7-carbothioate,

spiro[2H]-1-benzopyrane-2,1'(3'H)-isobenzofuran-3'-one,

4-[(3,4-dimethoxyphenyl)-3-(4-fluorophenyl)acryloyl]morpholine.

5 **Bactericides:**

bronopol, dichlorophen, nitrapyrin, nickel dimethyldithiocarbamate, kasugamycin, othilinone, furancarboxylic acid, oxytetracyclin, probenazole, streptomycin, tecloftalam, copper sulphate and other copper preparations.

Insecticides/acaricides/nematicides:

- 10 abamectin, acephate, acetamiprid, acrinathrin, alanycarb, aldicarb, aldoxycarb, alpha-cypermethrin, alphamethrin, amitraz, avermectin, AZ 60541, azadirachtin, azamethiphos, azinphos A, azinphos M, azocyclotin,

Bacillus popilliae, Bacillus sphaericus, Bacillus subtilis, Bacillus thuringiensis, baculoviruses, Beauveria bassiana, Beauveria tenella, bendiocarb, benfuracarb, bensultap, benzoximate,
15 betacyfluthrin, bifenazate, bifenthrin, bioethanomethrin, biopermethrin, bistrifluron, BPMC, bromophos A, bufencarb, buprofezin, butathiofos, butocarboxim, butylpyridaben,

- cadusafos, carbaryl, carbofuran, carbophenothion, carbosulfan, cartap, chloethocarb, chlorethoxyfos, chlorfenapyr, chlorfenvinphos, chlorfluazuron, chlormephos, chlorpyrifos, chlorpyrifos M, chlovaporthrin, chromafenozide, cis-resmethrin, cispermethrin, clocythrín,
20 cloethocarb, clofentezine, clothianidine, cyanophos, cycloprene, cycloprothrin, cyfluthrin, cyhalothrin, cyhexatin, cypermethrin, cyromazine,

deltamethrin, demeton M, demeton S, demeton-S-methyl, diafenthiuron, diazinon, dichlorvos, dicofol, diflubenzuron, dimethoate, dimethylvinphos, diofenolan, disulfoton, docusat-sodium, dofenapyn,

- 25 eflusilanate, emamectin, empenthrin, endosulfan, Entomopffthora spp., esfenvalerate, ethiofencarb, ethion, ethoprophos, etofenprox, etoxazole, etrimfos,

fenamiphos, fenazaquin, fenbutatin oxide, fenitrothion, fenothiocarb, fenoxacrim, fenoxycarb, fenpropathrin, fenpyrad, fenpyrithrin, fenpyroximate, fenvalerate, fipronil, fluozinam, fluazuron,

- flubrocycrinate, flucycloxuron, flucythrinate, flufenoxuron, flumethrin, flutenzine, fluvalinate, fonophos, fosmethilan, fosthiazate, fubfenprox, furathiocarb,
- granulosis viruses,
- halofenozide, HCH, heptenophos, hexaflumuron, hexythiazox, hydroprene,
- 5 imidacloprid, indoxacarb, isazofos, isofenphos, isoxathion, ivermectin,
- nuclear polyhedrosis viruses,
- lambda-cyhalothrin, lufenuron,
- malathion, mecarbam, metaldehyde, methamidophos, Metharhizium anisopliae, Metharhizium flavoviride, methidathion, methiocarb, methoprene, methomyl, methoxyfenozide, metolcarb,
- 10 metoxadiazone, mevinphos, milbemectin, milbemycin, monocrotophos,
- naled, nitenpyram, nithiazine, novaluron,
- omethoate, oxamyl, oxydemethon M,
- Paecilomyces fumosoroseus, parathion A, parathion M, permethrin, phenthoate, phorate, phosalone, phosmet, phosphamidon, phoxim, pirimicarb, pirimiphos A, pirimiphos M, profenofos,
- 15 promecarb, propargite, propoxur, prothiofos, prothoate, pymetrozine, pyraclofos, pyresmethrin, pyrethrum, pyridaben, pyridathion, pyrimidifen, pyriproxyfen,
- quinalphos,
- ribavirin,
- salithion, sebufos, silafluofen, spinosad, spirodiclofen, sulfotep, sulprofos,
- 20 tau-fluvalinate, tebufenozide, tebufenpyrad, tebupirimiphos, teflubenzuron, tefluthrin, temephos, temvinphos, terbufos, tetrachlorvinphos, tetradifon, theta-cypermethrin, thiacloprid, thiamethoxam, thiapronil, thiatrithos, thiocyclam hydrogen oxalate, thiodicarb, thiofanox, thuringiensin, traloccythrin, tralomethrin, triarathene, triazamate, triazophos, triazurone, trichlophenidine, trichlorfon, triflumuron, trimethacarb,
- 25 vamidothion, vaniliprole, Verticillium lecanii,
- YI 5302,

zeta-cypermethrin, zolaprofos

(1R-cis)-[5-(phenylmethyl)-3-furanyl]methyl 3-[(dihydro-2-oxo-3(2H)-furanylidene)methyl]-2,2-dimethylcyclopropanecarboxylate,

(3-phenoxyphenyl)methyl 2,2,3,3-tetramethylcyclopropanecarboxylate,

5 1-[(2-chloro-5-thiazolyl)methyl]tetrahydro-3,5-dimethyl-N-nitro-1,3,5-triazine-2(1H)-imine,

2-(2-chloro-6-fluorophenyl)-4-[4-(1,1-dimethylethyl)phenyl]-4,5-dihydrooxazole,

2-(acetyloxy)-3-dodecyl-1,4-naphthalenedione,

2-chloro-N-[[[4-(1-phenylethoxy)phenyl]amino]carbonyl]benzamide,

2-chloro-N-[[[4-(2,2-dichloro-1,1-difluoroethoxy)phenyl]amino]carbonyl]benzamide,

10 3-methylphenyl propylcarbamate,

4-[4-(4-ethoxyphenyl)-4-methylpentyl]-1-fluoro-2-phenoxybenzene,

4-chloro-2-(1,1-dimethylethyl)-5-[[2-(2,6-dimethyl-4-phenoxyphenoxy)ethyl]thio]-3(2H)-pyridazinone,

4-chloro-2-(2-chloro-2-methylpropyl)-5-[(6-iodo-3-pyridinyl)methoxy]-3(2H)-pyridazinone,

15 4-chloro-5-[(6-chloro-3-pyridinyl)methoxy]-2-(3,4-dichlorophenyl)-3(2H)-pyridazinone,

Bacillus thuringiensis strain EG-2348,

[2-benzoyl-1-(1,1-dimethylethyl)]hydrazobenzoic acid,

2,2-dimethyl-3-(2,4-dichlorophenyl)-2-oxo-1-oxaspiro[4.5]dec-3-en-4-yl butanoate,

[3-[(6-chloro-3-pyridinyl)methyl]-2-thiazolidinylidene]cyanamide,

20 dihydro-2-(nitromethylene)-2H-1,3-thiazine-3(4H)-carboxaldehyde,

ethyl [2-[[1,6-dihydro-6-oxo-1-(phenylmethyl)-4-pyridazinyl]oxy]ethyl]carbamate,

N-(3,4,4-trifluoro-1-oxo-3-butenyl)glycine,

N-(4-chlorophenyl)-3-[4-(difluoromethoxy)phenyl]-4,5-dihydro-4-phenyl-1H-pyrazole-1-carboxamide,

N-[(2-chloro-5-thiazolyl)methyl]-N'-methyl-N''-nitroguanidine,

N-methyl-N'-(1-methyl-2-propenyl)-1,2-hydrazinedicarbothioamide,

N-methyl-N'-2-propenyl-1,2-hydrazinedicarbothioamide,

O,O-diethyl [2-(dipropylamino)-2-oxoethyl]ethylphosphoramidothioate,

5 N-cyanomethyl-4-trifluoromethylnicotinamide,

3,5-dichloro-1-(3,3-dichloro-2-propenyloxy)-4-[3-(5-trifluoromethylpyridin-2-yloxy)propoxy]benzene.

A mixture with other known active compounds, such as herbicides, or with fertilizers and growth regulators is also possible.

10 When used as insecticides in their commercially available formulations and in the use forms prepared with these formulations, the active compounds according to the invention can furthermore exist in the form of a mixture with synergists. Synergists are compounds by which the activity of the active compounds is increased without it being necessary for the synergist added to be active itself.

The active compound content of the use forms prepared from the commercially available
15 formulations can vary within wide ranges. The active compound concentration of the use forms can be from 0.0000001 up to 95% by weight of active compound, preferably between 0.0001 and 1% by weight.

They are applied in a customary manner adapted to suit the use forms.

20 When used against hygiene pests and pests of stored products, the active compound or active compound combinations is distinguished by excellent residual action on wood and clay as well as good stability to alkali on limed substrates.

As already mentioned above, it is possible to treat all plants or their parts in accordance with the invention. In a preferred embodiment, wild plant species or plant varieties and plant cultivars which have been obtained by traditional biological breeding methods, such as hybridization or protoplast
25 fusion, and the parts of these varieties and cultivars are treated. In a further preferred embodiment, transgenic plants and plant cultivars which have been obtained by recombinant methods, if appropriate in combination with conventional methods (genetically modified organisms), and their parts are treated. The term "parts" or "parts of plants" or "plant parts" has been explained above.

Plants which are treated particularly preferably in accordance with the invention are those of the plant cultivars which are in each case commercially available or in use. Plant cultivars are understood as meaning plants with new traits which have been bred either by conventional breeding, by mutagenesis or by recombinant DNA techniques. They may take the form of cultivars, biotypes and
5 genotypes.

Depending on the plant species or plant cultivars, their location and growth conditions (soils, climate, vegetation period, nutrition), the treatment according to the invention may also result in superadditive ("synergistic") effects. Thus, for example, reduced application rates and/or a widened activity spectrum and/or an increase in the activity of the substances and compositions which can be used in
10 accordance with the invention, better plant growth, increased tolerance to high or low temperatures, increased tolerance to drought or to salinity in the water or soil, increased flowering performance, facilitated harvesting, accelerated maturation, higher yields, higher quality and/or better nutritional value of the harvested products, better storage characteristics and/or processibility of the harvested products are possible which exceed the effects which were actually to be expected.

15 The preferred transgenic plants or plant cultivars (those obtained by recombinant methods) to be treated in accordance with the invention include all those plants which, owing to the process of recombinant modification, were given genetic material which confers particular, advantageous, valuable traits to these plants. Examples of such properties are better plant growth, increased tolerance to high or low temperatures, increased tolerance to drought or to salinity in the water or
20 soil, increased flowering performance, facilitated harvesting, accelerated maturation, higher yields, higher quality and/or higher nutritional value of the harvested products, better storage characteristics and/or processibility of the harvested products. Further examples of such traits, examples which must be mentioned especially, are better defence of the plants against animal and microbial pests, such as against insects, mites, phytopathogenic fungi, bacteria and/or viruses and an increased tolerance of
25 the plants to certain herbicidal active compounds. Examples of transgenic plants which may be mentioned are the important crop plants, such as cereals (wheat, rice), maize, soybeans, potato, cotton, oilseed rape, beet, sugar cane and fruit plants (with the fruits apples, pears, citrus fruits and grapes), with particular emphasis on maize, soybeans, potatoes, cotton and oilseed rape. Traits which are especially emphasized are the increased defence of the plants against insects, owing to toxins
30 being formed in the plants, in particular toxins which are generated in the plants by the genetic material of *Bacillus thuringiensis* (for example by the genes CryIA(a), CryIA(b), CryIA(c), CryIIA, CryIIIA, CryIIIB2, Cry9c Cry2Ab, Cry3Bb and CryIF and their combinations; hereinbelow "Bt plants"). Other traits which are particularly emphasized are the increased defence of plants against fungi, bacteria and viruses by the systemic acquired resistance (SAR), systemin, phytoalexins,
35 elicitors and resistance genes and correspondingly expressed proteins and toxins. Other traits which

are especially emphasized are the increased tolerance of the plants to certain herbicidal active compounds, for example imidazolinones, sulphonylureas, glyphosate or phosphinothricin (for example "PAT" gene). The genes which confer the desired traits in each case may also be present in the transgenic plants in combination with one another. Examples of "Bt plants" which may be mentioned are maize cultivars, cotton cultivars, soybean cultivars and potato cultivars which are commercially available under the trade names YIELD GARD® (for example maize, cotton, soybeans), KnockOut® (for example maize), StarLink® (for example maize), Bollgard® (cotton), Nucleon® (cotton) and NewLeaf® (potato). Examples of herbicide-tolerant plants which may be mentioned are maize cultivars, cotton cultivars and soybean cultivars which are commercially available under the trade names Roundup Ready® (tolerance to glyphosate, for example maize, cotton, soybean), Liberty Link® (tolerance to phosphinothricin, for example oilseed rape), IMI® (tolerance to imidazolinones) and STS® (tolerance to sulphonylureas, for example maize). Herbicide-resistant plants (plants bred in a conventional manner for herbicide tolerance) which may be mentioned include also the varieties commercially available under the name Clearfield® (for example maize). Naturally, these statements also apply to plant cultivars having these genetic traits or genetic traits still to be developed, which plant cultivars will be developed and/or marketed in the future.

The plants listed can be treated particularly advantageously with the compounds according to the invention or the active compound mixtures according to the invention. The preferred ranges stated above for the active compounds and mixtures also apply to the treatment of these plants. Particular emphasis may be given to the treatment of plants with the compounds or mixtures specifically mentioned in the present text.

The active compounds or active compound combinations according to the invention are not only active against plant, hygiene and stored-product pests, but also, in the veterinary medicine sector, against animal parasites (ectoparasites), such as ixodid ticks, argasid ticks, scab mites, trombiculid mites, flies (stinging and sucking), parasitic fly larvae, lice, hair lice, bird lice and fleas. These parasites include:

From the order of the Anoplurida, for example, *Haematopinus* spp., *Linognathus* spp., *Pediculus* spp., *Phthirus* spp., *Solenopotes* spp.

From the order of the Mallophagida and the sub-orders Amblycerina and Ischnocerina, for example, *Trimenopon* spp., *Menopon* spp., *Trinoton* spp., *Bovicola* spp., *Werneckiella* spp., *Lepikentron* spp., *Damalina* spp., *Trichodectes* spp., *Felicola* spp.

From the order of the Diptera and the sub-orders Nematocerina and Brachycerina, for example, *Aedes* spp., *Anopheles* spp., *Culex* spp., *Simulium* spp., *Eusimulium* spp., *Phlebotomus* spp.,

Lutzomyia spp., Culicoides spp., Chrysops spp., Hybomitra spp., Atylotus spp., Tabanus spp., Haematopota spp., Philipomyia spp., Braula spp., Musca spp., Hydrotaea spp., Stomoxys spp., Haematobia spp., Morellia spp., Fannia spp., Glossina spp., Calliphora spp., Lucilia spp., Chrysomyia spp., Wohlfahrtia spp., Sarcophaga spp., Oestrus spp., Hypoderma spp., Gasterophilus
5 spp., Hippobosca spp., Lipoptena spp. and Melophagus spp.

From the order of the Siphonapterida, for example, Pulex spp., Ctenocephalides spp., Xenopsylla spp. and Ceratophyllus spp.

From the order of the Heteropterida, for example, Cimex spp., Triatoma spp., Rhodnius spp. and Panstrongylus spp.

10 From the order of the Blattarida, for example, Blatta orientalis, Periplaneta americana, Blattella germanica and Supella spp.

From the sub-class of the Acaria (Acarida) and the orders of the Meta- and Mesostigmata, for example, Argas spp., Ornithodoros spp., Otobius spp., Ixodes spp., Amblyomma spp., Boophilus spp., Dermacentor spp., Haemophysalis spp., Hyalomma spp., Rhipicephalus spp., Dermanyssus
15 spp., Raillietia spp., Pneumonyssus spp., Sternostoma spp. and Varroa spp.

From the order of the Actinedida (Prostigmata) and Acaridida (Astigmata), for example, Acarapis spp., Cheyletiella spp., Ornithocheyletia spp., Myobia spp., Psorergates spp., Demodex spp., Trombicula spp., Listrophorus spp., Acarus spp., Tyrophagus spp., Caloglyphus spp., Hypodectes spp., Pterolichus spp., Psoroptes spp., Chorioptes spp., Otodectes spp., Sarcoptes spp., Notoedres
20 spp., Knemidocoptes spp., Cytodites spp. and Laminosioptes spp.

The active compounds or active compound combinations according to the invention are also suitable for controlling arthropods which attack agricultural livestock, such as, for example, cattle, sheep, goats, horses, pigs, donkeys, camels, buffaloes, rabbits, chickens, turkeys, ducks, geese, honeybees, other domestic animals, such as, for example, dogs, cats, cage birds, aquarium fish, and
25 so-called experimental animals, such as, for example, hamsters, guinea-pigs, rats and mice. By combating these arthropods, it is intended to reduce deaths and decreased performances (in meat, milk, wool, hides, eggs, honey and the like), so that more economical and simpler animal keeping is made possible by using the active compounds according to the invention.

In the veterinary sector, the active compounds or active compound combinations according to the
30 invention are used in a known manner by enteral administration, for example in the form of tablets, capsules, drinks, drenches, granules, pastes, boli, the feed-through method, suppositories, by parenteral administration, such as, for example, by means of injections (intramuscular,

subcutaneous, intravenous, intraperitoneal and the like), implants, by nasal application, by dermal administration, for example in the form of dipping or bathing, spraying, pouring-on and spotting-on, washing, dusting, and with the aid of shaped articles which comprise active compound, such as collars, ear tags, tail marks, limb bands, halters, marking devices and the like.

- 5 When administered to livestock, poultry, domestic animals and the like, the active compounds or active compound combinations can be used as formulations (for example powders, emulsions, flowables) which comprise the active compounds in an amount of 1 to 80% by weight, either directly or after dilution by a factor of 100 to 10 000, or they may be used in the form of a chemical bath.
- 10 Furthermore, it has been found that the compounds or active compound combinations according to the invention have a potent insecticidal action against insects which destroy industrial materials.

The following insects may be mentioned by way of example and as being preferred, but without any limitation:

Beetles, such as

- 15 *Hylotrupes bajulus*, *Chlorophorus pilosis*, *Anobium punctatum*, *Xestobium rufovillosum*, *Ptilinus pecticornis*, *Dendrobium pertinex*, *Ernobius mollis*, *Priobium carpini*, *Lyctus brunneus*, *Lyctus africanus*, *Lyctus planicollis*, *Lyctus linearis*, *Lyctus pubescens*, *Troxylon aequale*, *Minthes rugicollis*, *Xyleborus spec.*, *Tryptodendron spec.*, *Apate monachus*, *Bostrychus capucins*, *Heterobostrychus brunneus*, *Sinoxylon spec.*, *Dinoderus minutus*.

- 20 Dermapterans, such as

Sirex juvencus, *Urocerus gigas*, *Urocerus gigas taignus*, *Urocerus augur*.

Termites, such as

- Kaloterms flavicollis*, *Cryptoterms brevis*, *Heteroterms indicola*, *Reticulitermes flavipes*, *Reticulitermes santonensis*, *Reticulitermes lucifugus*, *Mastoterms darwiniensis*, *Zootermopsis nevadensis*, *Coptoterms formosanus*.
- 25

Bristletails, such as *Lepisma saccharina*.

Industrial materials are to be understood as meaning, in the present context, non-live materials, such as, preferably, synthetic materials, glues, sizes, paper and board, leather, wood and timber products, and paint.

The materials to be very particularly preferably protected against attack by insects are wood and timber products.

Wood and timber products which can be protected by the composition according to the invention or mixtures comprising such a composition are to be understood as meaning, for example:

- 5 construction timber, wooden beams, railway sleepers, bridge components, jetties, wooden vehicles, boxes, pallets, containers, telephone poles, wood cladding, windows and doors made of wood, plywood, particle board, joiner's articles, or wood products which, quite generally, are used in the construction of houses or in joinery.

- 10 The active compounds or active compound combinations can be used as such, in the form of concentrates or generally customary formulations, such as powders, granules, solutions, suspensions, emulsions or pastes.

- 15 The formulations mentioned can be prepared in a manner known per se, for example by mixing the active compounds with at least one solvent or diluent, emulsifier, dispersant and/or binder or fixative, water repellent, if appropriate desiccants and UV stabilizers and, if appropriate, colorants and pigments and other processing auxiliaries.

The insecticidal compositions or concentrates used for the protection of wood and wooden materials comprise the active compound according to the invention in a concentration of 0.0001 to 95% by weight, in particular 0.001 to 60% by weight.

- 20 The amount of the compositions or concentrates employed depends on the species and the occurrence of the insects and on the medium. The optimum rate of application can be determined upon use in each case by a test series. However, in general, it suffices to employ 0.0001 to 20% by weight, preferably 0.001 to 10% by weight, of the active compound, based on the material to be protected.

- 25 The solvent and/or diluent used is an organochemical solvent or solvent mixture and/or an oily or oil-type organochemical solvent or solvent mixture of low volatility and/or a polar organochemical solvent or solvent mixture and/or water and, if appropriate, an emulsifier and/or wetting agent.

- 30 Organochemical solvents which are preferably employed are oily or oil-type solvents having an evaporation number of above 35 and a flashpoint of above 30°C, preferably above 45°C. Substances which are used as such oily and oil-type solvents which have low volatility and are insoluble in water are suitable mineral oils or their aromatic fractions, or mineral-oil-containing solvent mixtures, preferably white spirit, petroleum and/or alkylbenzene.

Substances which are advantageously used are mineral oils with a boiling range of 170 to 220°C, white spirit with a boiling range of 170 to 220°C, spindle oil with a boiling range of 250 to 350°C, petroleum or aromatics of boiling range 160 to 280°C, essence of turpentine and the like.

5 In a preferred embodiment, liquid aliphatic hydrocarbons with a boiling range of 180 to 210°C or high-boiling mixtures of aromatic and aliphatic hydrocarbons with a boiling range of 180 to 220°C and/or spindle oil and/or monochloronaphthalene, preferably α -monochloronaphthalene, are used.

10 The organic oily or oil-type solvents of low volatility having an evaporation number of above 35 and a flashpoint of above 30°C, preferably above 45°C, can be partially replaced by organochemical solvents of high or medium volatility, with the proviso that the solvent mixture also has an evaporation number of above 35 and a flashpoint of above 30°C, preferably above 45°C, and that the insecticide/fungicide mixture is soluble or emulsifiable in this solvent mixture.

15 In a preferred embodiment, part of the organochemical solvent or solvent mixture is replaced by an aliphatic polar organochemical solvent or solvent mixture. Substances which are preferably used are aliphatic organochemical solvents having hydroxyl and/or ester and/or ether groups, such as, for example, glycol ethers, esters and the like.

20 The organochemical binders used within the scope of the present invention are the synthetic resins and/or binding drying oils which are known per se and can be diluted with water and/or are soluble or dispersible or emulsifiable in the organochemical solvents employed, in particular binders composed of, or comprising, an acrylate resin, a vinyl resin, for example polyvinyl acetate, polyester resin, polycondensation or polyaddition resin, polyurethane resin, alkyd resin or modified alkyd resin, phenol resin, hydrocarbon resin, such as indene/cumarone resin, silicone resin, drying vegetable and/or drying oils and/or physically drying binders based on a natural and/or synthetic resin.

25 The synthetic resin used as the binder can be employed in the form of an emulsion, dispersion or solution. Up to 10% by weight of bitumen or bituminous substances can also be used as binders. In addition, colorants, pigments, water repellents, odour-masking substances and inhibitors or anticorrosives known per se and the like can also be employed.

30 The composition or the concentrate preferably comprises, in accordance with the invention, at least one alkyd resin or modified alkyd resin and/or a drying vegetable oil as the organochemical binder. Preferably used according to the invention are alkyd resins with an oil content of over 45% by weight, preferably 50 to 68% by weight.

All or some of the abovementioned binder can be replaced by a fixative (mixture) or a plasticizer (mixture). These additives are intended to prevent volatilization of the active compounds and crystallization or precipitation. They preferably replace 0.01 to 30% of the binder (based on 100% of binder employed).

5

The plasticizers are from the chemical classes of the phthalic esters, such as dibutyl phthalate, dioctyl phthalate or benzyl butyl phthalate, the phosphoric esters, such as tributyl phosphate, the adipic esters, such as di-(2-ethylhexyl) adipate, the stearates, such as butyl stearate or amyl stearate, the oleates, such as butyl oleate, the glycerol ethers or relatively high-molecular-weight glycol ethers, glycerol esters and p-toluenesulphonic esters.

10

Fixatives are chemically based on polyvinyl alkyl ethers, such as, for example, polyvinyl methyl ether, or ketones, such as benzophenone or ethylenebenzophenone.

Particularly suitable as a solvent or diluent is also water, if appropriate as a mixture with one or more of the abovementioned organochemical solvents or diluents, emulsifiers and dispersants.

15

Particularly effective protection of wood is achieved by large-scale industrial impregnation processes, for example vacuum, double-vacuum or pressure processes.

20

If appropriate, the ready-to-use compositions can additionally comprise other insecticides and, if appropriate, additionally one or more fungicides.

Suitable additional components which may be admixed are, preferably, the insecticides and fungicides mentioned in WO 94/29 268. The compounds mentioned in that document are expressly part of the present application.

25

Very particularly preferred components which may be admixed are insecticides, such as chlorpyrifos, phoxim, silafluofin, alphamethrin, cyfluthrin, cypermethrin, deltamethrin, permethrin, imidacloprid, NI-25, flufenoxuron, hexaflumuron, transfluthrin, thiacloprid, methoxyphenoxid and triflumuron,

30

and fungicides, such as epoxyconazole, hexaconazole, azaconazole, propiconazole, tebuconazole, cyproconazole, metconazole, imazalil, dichlofluanid, tolylfluanid, 3-iodo-2-propynylbutyl carbamate, N-octylisothiazolin-3-one and 4,5-dichloro-N-octylisothiazolin-3-one.

The compounds or active compound combinations according to the invention can at the same time be employed for protecting objects which come into contact with salt water or brackish water, in particular hulls, screens, nets, buildings, moorings and signalling systems, against fouling.

5 Fouling by sessile Oligochaeta, such as Serpulidae, and by shells and species from the Ledamorpha group (goose barnacles), such as various Lepas and Scalpellum species, or by species from the Balanomorpha group (acorn barnacles), such as Balanus or Pollicipes species, increases the frictional drag of ships and, as a consequence, leads to a marked increase in operation costs owing to higher energy consumption and additionally frequent residence in the dry dock.

10 Apart from fouling by algae, for example Ectocarpus sp. and Ceramium sp., fouling by sessile Entomostraka groups, which come under the generic term Cirripedia (cirriped crustaceans), is of particular importance.

Surprisingly, it has now been found that the compounds according to the invention, alone or in combination with other active compounds, have an outstanding antifouling action.

15 Using the compounds according to the invention, alone or in combination with other active compounds, allows the use of heavy metals such as, for example, in bis(trialkyltin) sulphides, tri-*n*-butyltin laurate, tri-*n*-butyltin chloride, copper(I) oxide, triethyltin chloride, tri-*n*-butyl-(2-phenyl-4-chlorophenoxy)tin, tributyltin oxide, molybdenum disulphide, antimony oxide, polymeric butyl titanate, phenyl(bispyridine)bismuth chloride, tri-*n*-butyltin fluoride, manganese ethylenebisthiocarbamate, zinc dimethyldithiocarbamate, zinc ethylenebisthiocarbamate, zinc salts and copper

20 salts of 2-pyridinethiol 1-oxide, bisdimethyldithiocarbamoylzinc ethylene-bisthiocarbamate, zinc oxide, copper(I) ethylene-bisdithiocarbamate, copper thiocyanate, copper naphthenate and tri-butyltin halides to be dispensed with, or the concentration of these compounds to be substantially reduced.

25 If appropriate, the ready-to-use antifouling paints can additionally comprise other active compounds, preferably algicides, fungicides, herbicides, molluscicides, or other antifouling active compounds.

Preferably suitable components in combination with the antifouling compositions according to the invention are:

30 algicides such as

2-*tert*-butylamino-4-cyclopropylamino-6-methylthio-1,3,5-triazine, dichlorophen, diuron, endothal, fentin acetate, isoproturon, methabenzthiazuron, oxyfluorfen, quinoclamine and terbutryn;

fungicides such as

benzo[*b*]thiophenecarboxylic acid cyclohexylamide S,S-dioxide, dichlofluanid, fluorfolpet, 3-iodo-2-propynyl butylcarbamate, tolylfluanid and azoles such as

5 azaconazole, cyproconazole, epoxyconazole, hexaconazole, metconazole, propiconazole and tebuconazole;

molluscicides such as

fentin acetate, metaldehyde, methiocarb, niclosamid, thiodicarb and trimethacarb;

or conventional antifouling active compounds such as

10 4,5-dichloro-2-octyl-4-isothiazolin-3-one, diiodomethylparatryl sulphone, 2-(N,N-dimethylthiocarbamoylthio)-5-nitrothiazyl, potassium, copper, sodium and zinc salts of 2-pyridinethiol 1-oxide, pyridine-triphenylborane, tetrabutyl-distannoxane, 2,3,5,6-tetrachloro-4-(methylsulphonyl)pyridine, 2,4,5,6-tetrachloroisophthalonitrile, tetramethylthiuram disulphide and 2,4,6-trichlorophenylmaleimide.

15 The antifouling compositions used comprise the active compound according to the invention of the compounds according to the invention in a concentration of 0.001 to 50% by weight, in particular 0.01 to 20% by weight.

Moreover, the antifouling compositions according to the invention comprise the customary components such as, for example, those described in Ungerer, *Chem. Ind.* 1985, 37, 730-732 and Williams, *Antifouling Marine Coatings*, Noyes, Park Ridge, 1973.

20 Besides the algicidal, fungicidal, molluscicidal active compounds and insecticidal active compounds according to the invention, antifouling paints comprise, in particular, binders.

25 Examples of recognized binders are polyvinyl chloride in a solvent system, chlorinated rubber in a solvent system, acrylic resins in a solvent system, in particular in an aqueous system, vinyl chloride/vinyl acetate copolymer systems in the form of aqueous dispersions or in the form of organic solvent systems, butadiene/styrene/acrylonitrile rubbers, drying oils such as linseed oil, resin esters or modified hardened resins in combination with tar or bitumens, asphalt and epoxy compounds, small amounts of chlorine rubber, chlorinated polypropylene and vinyl resins.

If appropriate, paints also comprise inorganic pigments, organic pigments or colorants which are preferably insoluble in salt water. Paints may furthermore comprise materials such as rosin to

allow controlled release of the active compounds. Furthermore, the paints may comprise plasticizers, modifiers which affect the rheological properties and other conventional constituents. The compounds according to the invention or the abovementioned mixtures may also be incorporated into self-polishing antifouling systems.

- 5 The active compounds or active compound combinations are also suitable for controlling animal pests, in particular insects, arachnids and mites, which are found in enclosed spaces such as, for example, dwellings, factory halls, offices, vehicle cabins and the like. They can be employed in domestic insecticide products for controlling these pests alone or in combination with other active compounds and auxiliaries. They are active against sensitive and resistant species and against all
10 development stages. These pests include:

From the order of the Scorpionidea, for example, *Buthus occitanus*.

- From the order of the Acarina, for example, *Argas persicus*, *Argas reflexus*, *Bryobia* spp., *Dermanyssus gallinae*, *Glyciphagus domesticus*, *Ornithodoros moubat*, *Rhipicephalus sanguineus*, *Trombicula alfreddugesi*, *Neutrombicula autumnalis*, *Dermatophagoides pteronissimus*,
15 *Dermatophagoides forinae*.

From the order of the Araneae, for example, *Aviculariidae*, *Araneidae*.

- From the order of the Opiliones, for example, *Pseudoscorpiones chelifer*, *Pseudoscorpiones cheiridium*, *Opiliones phalangium*.
20

From the order of the Isopoda, for example, *Oniscus asellus*, *Porcellio scaber*.

From the order of the Diplopoda, for example, *Blaniulus guttulatus*, *Polydesmus* spp.

From the order of the Chilopoda, for example, *Geophilus* spp.

- 25 From the order of the Zygentoma, for example, *Ctenolepisma* spp., *Lepisma saccharina*, *Lepismodes inquilinus*.

- From the order of the Blattaria, for example, *Blatta orientalis*, *Blattella germanica*, *Blattella asahinai*, *Leucophaea maderae*, *Panchlora* spp., *Parcoblatta* spp., *Periplaneta australasiae*,
30 *Periplaneta americana*, *Periplaneta brunnea*, *Periplaneta fuliginosa*, *Supella longipalpa*.

From the order of the Saltatoria, for example, *Acheta domesticus*.

From the order of the Dermaptera, for example, *Forficula auricularia*.

From the order of the Isoptera, for example, *Kaloterme* spp., *Reticuliterme* spp.

From the order of the Psocoptera, for example, *Lepinatus* spp., *Liposcelis* spp.

5

From the order of the Coleoptera, for example, *Anthrenus* spp., *Attagenus* spp., *Dermestes* spp., *Latheticus oryzae*, *Necrobia* spp., *Ptinus* spp., *Rhizopertha dominica*, *Sitophilus granarius*, *Sitophilus oryzae*, *Sitophilus zeamais*, *Stegobium paniceum*.

10 From the order of the Diptera, for example, *Aedes aegypti*, *Aedes albopictus*, *Aedes taeniorhynchus*, *Anopheles* spp., *Calliphora erythrocephala*, *Chrysosoma pluvialis*, *Culex quinquefasciatus*, *Culex pipiens*, *Culex tarsalis*, *Drosophila* spp., *Fannia canicularis*, *Musca domestica*, *Phlebotomus* spp., *Sarcophaga carnaria*, *Simulium* spp., *Stomoxys calcitrans*, *Tipula paludosa*.

15 From the order of the Lepidoptera, for example, *Achroia grisella*, *Galleria mellonella*, *Plodia interpunctella*, *Tinea cloacella*, *Tinea pellionella*, *Tineola bisselliella*.

From the order of the Siphonaptera, for example, *Ctenocephalides canis*, *Ctenocephalides felis*, *Pulex irritans*, *Tunga penetrans*, *Xenopsylla cheopis*.

20 From the order of the Hymenoptera, for example, *Camponotus herculeanus*, *Lasius fuliginosus*, *Lasius niger*, *Lasius umbratus*, *Monomorium pharaonis*, *Paravespula* spp., *Tetramorium caespitum*.

From the order of the Anoplura, for example, *Pediculus humanus capitis*, *Pediculus humanus corporis*, *Phthirus pubis*.

25 From the order of the Heteroptera, for example, *Cimex hemipterus*, *Cimex lectularius*, *Rhodinus prolixus*, *Triatoma infestans*.

They are used in the household insecticides sector alone or in combination with other suitable active compounds such as phosphoric esters, carbamates, pyrethroids, growth regulators or active compounds from other known classes of insecticides.

30

They are used in aerosols, pressure-free spray products, for example pump and atomizer sprays, automatic fogging systems, foggers, foams, gels, evaporator products with evaporator tablets made of cellulose or polymer, liquid evaporators, gel and membrane evaporators, propeller-driven

evaporators, energy-free, or passive, evaporation systems, moth papers, moth bags and moth gels, as granules or dusts, in baits for spreading or in bait stations.

The active compounds or active compound combinations according to the invention can also be used as defoliants, desiccants, haulm killers and, in particular, as weed killers. Weeds in the
 5 broadest sense are understood as meaning all plants which grow at locations where they are undesired. Whether the substances according to the invention act as nonselective or selective herbicides depends essentially on the application rate.

The active compounds or active compound combinations according to the invention can be used for example in the following plants:

- 10 Dicotyledonous weeds of the genera: Abutilon, Amaranthus, Ambrosia, Anoda, Anthemis, Aphanes, Atriplex, Bellis, Bidens, Capsella, Carduus, Cassia, Centaurea, Chenopodium, Cirsium, Convolvulus, Datura, Desmodium, Emex, Erysimum, Euphorbia, Galeopsis, Galinsoga, Galium, Hibiscus, Ipomoea, Kochia, Lamium, Lepidium, Lindernia, Matricaria, Mentha, Mercurialis, Mullugo, Myosotis, Papaver, Pharbitis, Plantago, Polygonum, Portulaca, Ranunculus, Raphanus,
 15 Rorippa, Rotala, Rumex, Salsola, Senecio, Sesbania, Sida, Sinapis, Solanum, Sonchus, Sphenoclea, Stellaria, Taraxacum, Thlaspi, Trifolium, Urtica, Veronica, Viola, Xanthium.

Dicotyledonous crops of the genera: Arachis, Beta, Brassica, Cucumis, Cucurbita, Helianthus, Daucus, Glycine, Gossypium, Ipomoea, Lactuca, Linum, Lycopersicon, Nicotiana, Phaseolus, Pisum, Solanum, Vicia.

- 20 Monocotyledonous weeds of the genera: Aegilops, Agropyron, Agrostis, Alopecurus, Apera, Avena, Brachiaria, Bromus, Cenchrus, Commelina, Cynodon, Cyperus, Dactyloctenium, Digitaria, Echinochloa, Eleocharis, Eleusine, Eragrostis, Eriochloa, Festuca, Fimbristylis, Heteranthera, Imperata, Ischaemum, Leptochloa, Lolium, Monochoria, Panicum, Paspalum, Phalaris, Phleum, Poa, Rottboellia, Sagittaria, Scirpus, Setaria, Sorghum.

- 25 Monocotyledonous crops of the genera: Allium, Ananas, Asparagus, Avena, Hordeum, Oryza, Panicum, Saccharum, Secale, Sorghum, Triticale, Triticum, Zea.

However, the use of the active compounds or active compound combinations according to the invention is in no way restricted to these genera, but extends in the same manner to other plants.

- Depending on the concentration, the active compounds or active compound combinations
 30 according to the invention are suitable for the nonselective weed control on, for example, industrial terrains and railway tracks and on paths and locations with and without trees. Likewise

the active compounds according to the invention can be employed for controlling weeds in perennial crops, for example forests, ornamental tree plantings, orchards, vineyards, citrus groves, nut orchards, banana plantations, coffee plantations, tea plantations, rubber plantations, oil palm plantations, cocoa plantations, soft fruit plantings and hop fields, on lawns, turf and pastureland, and for the selective control of weeds in annual crops.

The compounds or active compound combinations according to the invention have strong herbicidal activity and a broad activity spectrum when used on the soil and on aerial plant parts. To a certain extent, they are also suitable for the selective control of monocotyledonous and dicotyledonous weeds in monocotyledonous and dicotyledonous crops, both pre- and post-emergence.

At certain concentrations or application rates, the active compounds or active compound combinations according to the invention can also be employed for controlling animal pests and fungal or bacterial plant diseases. If appropriate, they can also be used as intermediates or precursors for the synthesis of other active compounds.

The active compounds or active compound combinations can be converted into the customary formulations, such as solutions, emulsions, wettable powders, suspensions, powders, dusting agents, pastes, soluble powders, granules, suspoemulsion concentrates, natural and synthetic materials impregnated with active compound, and microcapsules in polymeric substances.

These formulations are produced in a known manner, for example by mixing the active compounds with extenders, that is liquid solvents and/or solid carriers, optionally with the use of surfactants, that is emulsifiers and/or dispersants and/or foam-formers.

If the extender used is water, it is also possible to use, for example, organic solvents as auxiliary solvents. Suitable liquid solvents are essentially: aromatics, such as xylene, toluene or alkylnaphthalenes, chlorinated aromatics and chlorinated aliphatic hydrocarbons, such as chlorobenzenes, chloroethylenes or methylene chloride, aliphatic hydrocarbons, such as cyclohexane or paraffins, for example mineral oil fractions, mineral and vegetable oils, alcohols, such as butanol or glycol, and also their ethers and esters, ketones, such as acetone, methyl ethyl ketone, methyl isobutyl ketone or cyclohexanone, strongly polar solvents, such as dimethylformamide and dimethyl sulphoxide, and also water.

Suitable solid carriers are: for example ammonium salts and ground natural minerals, such as kaolins, clays, talc, chalk, quartz, attapulgite, montmorillonite or diatomaceous earth, and ground synthetic minerals, such as finely divided silica, alumina and silicates, suitable solid carriers for granules are:

for example crushed and fractionated natural rocks such as calcite, marble, pumice, sepiolite and dolomite, and also synthetic granules of inorganic and organic meals, and granules of organic material such as sawdust, coconut shells, maize cobs and tobacco stalks; suitable emulsifiers and/or foam-formers are: for example non-ionic and anionic emulsifiers, such as polyoxyethylene fatty acid esters, polyoxyethylene fatty alcohol ethers, for example alkylaryl polyglycol ethers, alkylsulphonates, alkyl sulphates, arylsulphonates and protein hydrolysates; suitable dispersants are: for example lignosulphite waste liquors and methylcellulose.

Tackifiers such as carboxymethylcellulose and natural and synthetic polymers in the form of powders, granules or latices, such as gum arabic, polyvinyl alcohol and polyvinyl acetate, and also natural phospholipids, such as cephalins and lecithins, and synthetic phospholipids, can be used in the formulations. Other possible additives are mineral and vegetable oils.

It is possible to use colorants such as inorganic pigments, for example iron oxide, titanium oxide and Prussian Blue, and organic dyestuffs, such as alizarin dyestuffs, azo dyestuffs and metal phthalocyanine dyestuffs, and trace nutrients such as salts of iron, manganese, boron, copper, cobalt, molybdenum and zinc.

The formulations generally comprise between 0.1 and 95 per cent by weight of active compound, preferably between 0.5 and 90%.

The active compounds according to the invention, as such or in their formulations, can also be used for weed control purposes as a mixture with known herbicides and/or with substances which improve crop plant compatibility ("safeners"), ready mixes or tank mixes being possible. Mixtures with herbicide products which contain one or more known herbicides and a safener are hence also possible.

Herbicides which are suitable for the mixtures are known herbicides, for example acetochlor, acifluorfen (-sodium), aclonifen, alachlor, alloxymid (-sodium), ametryne, amicarbazone, amidochlor, amidosulfuron, anilofos, asulam, atrazine, azafenidin, azimsulfuron, beflubutamid, benazolin (-ethyl), benfuresate, bensulfuron (-methyl), bentazone, benzfendizone, benzobicyclon, benzofenap, benzoylprop (-ethyl), bialaphos, bifenox, bispyribac (-sodium), bromobutide, bromofenoxim, bromoxynil, butachlor, butafenacil (-allyl), butoxydim, butylate, cafenstrole, caloxydim, carbetamide, carfentrazone (-ethyl), chlomethoxyfen, chloramben, chloridazon, chlorimuron (-ethyl), chlornitrofen, chlorsulfuron, chlortoluron, cinidon (-ethyl), cinmethylin, cinosulfuron, clefoxydim, clethodim, clodinafop (-propargyl), clomazone, clomeprop, clopyralid, clopyrasulfuron (-methyl), cloransulam (-methyl), cumyluron, cyanazine, cybutryne, cycloate,

cyclosulfamuron, cycloxydim, cyhalofop (-butyl), 2,4-D, 2,4-DB, desmedipham, diallate, dicamba, dichlorprop (-P), diclofop (-methyl), diclosulam, diethatyl (-ethyl), difenzoquat, diflufenican, diflufenzopyr, dimefuron, dimepiperate, dimethachlor, dimethametryn, dimethenamid, dimexyflam, dinitramine, diphenamid, diquat, dithiopyr, diuron, dymron, epropodan, EPTC, esprocarb, ethalfluralin, ethametsulfuron(-methyl), ethofumesate, ethoxyfen, ethoxysulfuron, etobenzanid, fenoxa-
 5 prop (-P-ethyl), fentrazamide, flamprop (-isopropyl, -isopropyl-L, -methyl), flazasulfuron, florasulam, fluazifop (-P-butyl), fluazolate, flucarbazone (-sodium), flufenacet, flumetsulam, flumiclorac (-pentyl), flumioxazin, flumipropyn, flumetsulam, fluometuron, fluorochloridone, fluoroglycofen (-ethyl), flupoxam, flupropacil, flurpysulfuron (-methyl, -sodium), flurenol (-butyl),
 10 fluridone, fluroxypyr (-butoxypropyl, -meptyl), flurprimidol, flurtamone, fluthiacet (-methyl), fluthiamide, fomesafen, foramsulfuron, glufosinate (-ammonium), glyphosate (-isopropylammonium), halosafen, haloxyfop (-ethoxyethyl, -P-methyl), hexazinone, imazamethabenz (-methyl), imazamethapyr, imazamox, imazapic, imazapyr, imazaquin, imazethapyr, imazosulfuron, iodosulfuron (-methyl, -sodium), ioxynil, isopropalin, isoproturon, isouron, isoxaben, isoxachlortole, isoxa-
 15 flutole, isoxapyrifop, lactofen, lenacil, linuron, MCPA, mecoprop, mefenacet, mesosulfurone, mesotrione, metamitron, metazachlor, methabenzthiazuron, metobenzuron, metobromuron, (alpha-) metolachlor, metosulam, metoxuron, metribuzin, metsulfuron (-methyl), molinate, monolinuron, naproanilide, napropamide, neburon, nicosulfuron, norflurazon, orbencarb, oryzalin, oxadiargyl, oxadiazon, oxasulfuron, oxaziclomefone, oxyfluorfen, paraquat, pelargonic acid, pen-
 20 dimethalin, pendralin, pentoxazone, phenmedipham, picolinafen, pinoxaden, piperophos, pretilachlor, primisulfuron (-methyl), profluazol, prometryn, propachlor, propanil, propaquizafop, propisochlor, propoxycarbazone (-sodium), propyzamide, prosulfocarb, prosulfuron, pyraflufen (-ethyl), pyrazogyl, pyrazolate, pyrazosulfuron (-ethyl), pyrazoxyfen, pyribenzoxim, pyributicarb, pyridate, pyridatol, pyriftalide, pyriminobac (-methyl), pyriothiobac (-sodium), quinchlorac, quin-
 25 merac, quinoclamine, quizalofop (-P-ethyl, -P-tefuryl), rimsulfuron, sethoxydim, simazine, simetryn, sulcotrione, sulfentrazone, sulfometuron (-methyl), sulfosate, sulfosulfuron, tebutam, tebuthiuron, tepraloxym, terbuthylazine, terbutryn, thenylchlor, thiafluamide, thiazopyr, thidiazimin, thifensulfuron (-methyl), thiobencarb, tiocarbazil, tralkoxydim, triallate, triasulfuron, tribenuron (-methyl), triclopyr, tridiphane, trifluralin, trifloxysulfuron, triflusulfuron (-methyl), tritosulf-
 30 uron.

A mixture with other known active compounds, such as fungicides, insecticides, acaricides, nematocides, bird repellents, plant nutrients and soil conditioners, is also possible.

The active compounds or active compound combinations can be applied as such, in the form of their formulations or the use forms prepared therefrom by further dilution, such as ready-to-use

solutions, suspensions, emulsions, powders, pastes and granules. They are applied in the customary manner, for example by pouring, spraying, atomizing, spreading.

The active compounds or active compound combinations according to the invention can be applied both before and after plant emergence. They can also be incorporated into the soil prior to sowing.

- 5 The application rate of active compound can vary within a substantial range. Essentially, it depends on the nature of the desired effect. In general, the application rates are between 1 g and 10 kg of active compound per hectare of soil area, preferably between 5 g and 5 kg per ha.

The advantageous effect of the compatibility with crop plants of the active compound combinations according to the invention is particularly pronounced at certain concentration ratios.

- 10 However, the weight ratios of the active compounds in the active compound combinations can be varied within relatively wide ranges. In general, from 0.001 to 1000 parts by weight, preferably from 0.01 to 100 parts by weight, particularly preferably 0.05 to 20 parts by weight, of one of the compounds which improves crop plant compatibility (antidotes/safeners) mentioned above under (b') are present per part by weight of active compound of the formula (I).

- 15 The active compound combinations according to the invention are generally applied in the form of finished formulations. However, the active compounds contained in the active compound combinations can, as individual formulations, also be mixed during use, i.e. be applied in the form of tank mixes.

- For certain applications, in particular by the post-emergence method, it may furthermore be
20 advantageous to include, as further additives in the formulations, mineral or vegetable oils which are compatible with plants (for example commercial preparation "Rako Bino!"), or ammonium salts, such as, for example, ammonium sulphate or ammonium thiocyanate.

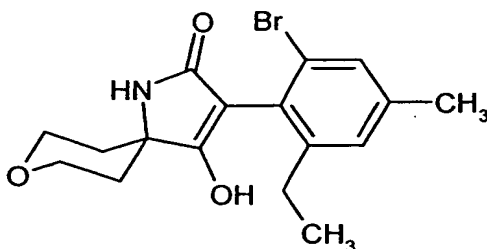
- The novel active compound combinations can be used as such, in the form of their formulations or the use forms prepared therefrom by further dilution, such as ready-to-use solutions, suspensions,
25 emulsions, powders, pastes and granules. Application is in the customary manner, for example by watering, spraying, atomizing, dusting or scattering.

- The application rates of the active compound combinations according to the invention can be varied within a certain range; they depend, inter alia, on the weather and on soil factors. In general, the application rates are between 0.001 and 5 kg per ha, preferably between 0.005 and 2 kg per ha,
30 particularly preferably between 0.01 and 0.5 kg per ha.

The active compound combinations according to the invention can be applied before and after emergence of the plants, that is to say by the pre-emergence and post-emergence method.

Depending on their properties, the safeners to be used according to the invention can be used for pretreating the seed of the crop plant (seed dressing) or can be introduced into the seed furrows
5 prior to sowing or be used separately prior to the herbicide or together with the herbicide, before or after emergence of the plants.

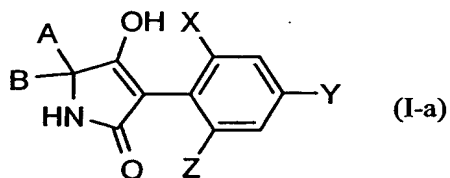
Preparation and use of the active compounds according to the invention are illustrated in the examples below.

Examples**Example I-a-1**

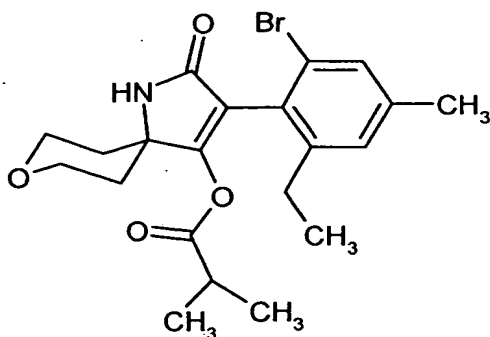
Under argon, 5.2 g of potassium tert-butoxide, 95% pure (44 mmol), in 10 ml of dimethylacetamide
 5 are initially charged in a 100 ml three-necked flask fitted with thermometer and reflux condenser. At
 40-50°C, 7.9 g of the compound of Example II-1 (19.8 mmol) in 16 ml of dimethylacetamide are
 added dropwise. The mixture is stirred at 50°C for 1 hour. The reaction solution is added to 100 ml of
 ice-water, and the pH of the mixture is, at 0-10°C, adjusted with conc. hydrochloric acid to pH = 2.
 The precipitate is filtered off with suction. This is followed by column-chromatographic purification
 10 on silica gel (dichloromethane:ethyl acetate, 5:3).

Yield: 6.4 g, 88.1% of theory, m.p. 314°C.

Analogously to Example (I-a-1) and in accordance with the general statements on the preparation, the
 following compounds of the formula (I-a) are obtained



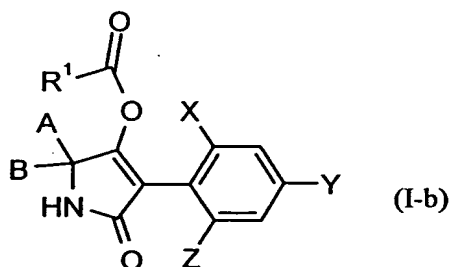
Ex. No.	X	Y	Z	A	B	m.p.°C	isomer
I-a-2	Br	CH ₃	C ₂ H ₅	-(CH ₂) ₅ -		202	-
I-a-3	Br	CH ₃	C ₂ H ₅	-(CH ₂) ₂ -CHOCH ₃ -(CH ₂) ₂ -		235	β
I-a-4	Cl	CH ₃	C ₂ H ₅	-(CH ₂) ₂ -CHOCH ₃ -(CH ₂) ₂ -		228	β
I-a-5	Br	CH ₃	C ₂ H ₅	-(CH ₂) ₂ -CHOC ₂ H ₅ -(CH ₂) ₂ -		170	β
I-a-6	Br	CH ₃	C ₂ H ₅	-(CH ₂) ₂ -CHOC ₃ H ₇ -(CH ₂) ₂ -		134	β

Example I-b-1

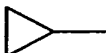
- Under argon, 0.73 g of the compound of Example I-a-1 in 30 ml of anhydrous ethyl acetate and 0.2 g of triethylamine (2 mmol) = 0.28 ml are initially charged in a 100 ml three-necked flask with thermometer and reflux condenser, 10 mg of Steglich base are added and, at 60°C, 0.22 g (0.002 mol) of isobutyryl chloride in 2 ml of anhydrous ethyl acetate are added. The mixture is stirred under reflux for 1 hour, and the reaction is monitored by thin-layer chromatography. The solvent is distilled off and the residue is purified by silica gel column chromatography (hexane:ethyl acetate, 8:2).

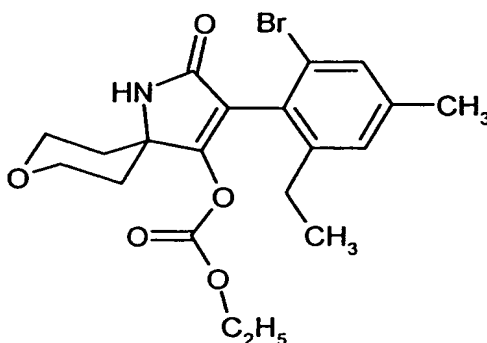
Yield: 0.85 g (93.8% of theory), m.p. 238°C.

- 10 Analogously to Example (I-b-1) and in accordance with the general statements on the preparation, the following compounds of the formula (I-b) are obtained



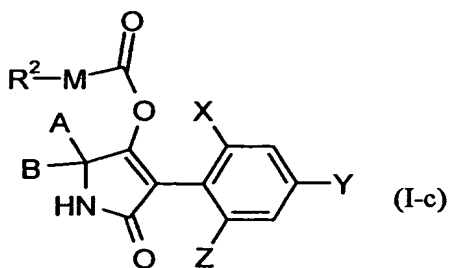
Ex. No.	X	Y	Z	A	B	R ¹	m.p.°C	isomer
I-b-2	Br	CH ₃	C ₂ H ₅	-(CH ₂) ₅ -		H ₃ CO-CH ₂ -	164	-
I-b-3	Br	CH ₃	C ₂ H ₅	-(CH ₂) ₅ -		i-C ₃ H ₇	205	-
I-b-4	Br	CH ₃	C ₂ H ₅	-(CH ₂) ₅ -		t-C ₄ H ₉	144	-
I-b-5	Br	CH ₃	C ₂ H ₅	-(CH ₂) ₂ -CHOCH ₃ - (CH ₂) ₂ -		H ₃ C-O-CH ₂ -	172-175	β
I-b-6	Br	CH ₃	C ₂ H ₅	-(CH ₂) ₂ -O-(CH ₂) ₂ -		C ₂ H ₅ -O-CH ₂ -	192	-

Ex. No.	X	Y	Z	A	B	R ¹	m.p.°C	isomer
I-b-7	Br	CH ₃	C ₂ H ₅	-(CH ₂) ₂ -CHOCH ₃ - (CH ₂) ₂ -			224	β
I-b-8	Br	CH ₃	C ₂ H ₅	-(CH ₂) ₂ -CHOCH ₃ - (CH ₂) ₂ -		i-C ₃ H ₇	216	β

Example I-c-1

- Under argon, 0.733 g of the compound of Example I-a-1 in 30 ml of anhydrous dichloromethane and 0.28 ml (2 mmol) of triethylamine are initially charged in a 100 ml three-necked flask fitted with thermometer and reflux condenser, and 0.22 g (0.002 mol) of ethyl chloroformate in 2 ml of anhydrous dichloromethane is added at 20°C. The mixture is stirred at room temperature for 1 hour, and the reaction is monitored by thin-layer chromatography. The solvent is distilled off and the residue is purified by silica gel column chromatography (hexane:ethyl acetate, 8:2).
- 10 Yield: 0.85 g (97% of theory), m.p. 196°C.

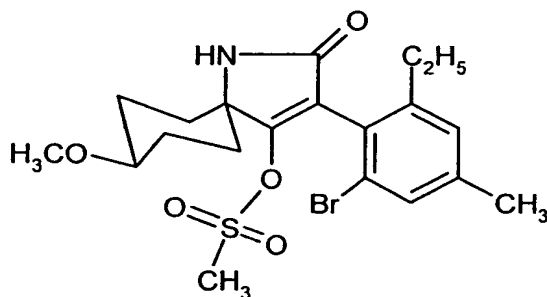
Analogously to Example (I-c-1) and in accordance with the general statements on the preparation, the following compounds of the formula (I-c) are obtained



Ex. No.	X	Y	Z	A	B	M	R ²	m.p.°C	iso-mer
I-c-2	Br	CH ₃	C ₂ H ₅	-(CH ₂) ₅ -		O	C ₂ H ₅	*	-
I-c-3	Br	CH ₃	C ₂ H ₅	-(CH ₂) ₂ -CHOCH ₃ -(CH ₂) ₂ -		O	C ₂ H ₅	185	β
I-c-4	Cl	CH ₃	C ₂ H ₅	-(CH ₂) ₂ -CHOCH ₃ -(CH ₂) ₂ -		O	C ₂ H ₅	oil	β
I-c-5	Br	CH ₃	C ₂ H ₅	-(CH ₂) ₂ -CHOC ₃ H ₇ -(CH ₂) ₂ -		O	C ₂ H ₅	209	β
I-c-6	Br	CH ₃	C ₂ H ₅	-(CH ₂) ₂ -CHOC ₂ H ₅ -(CH ₂) ₂ -		O	C ₂ H ₅	187	β
I-c-7	Br	CH ₃	C ₂ H ₅	-(CH ₂) ₂ -CHOCH ₃ -(CH ₂) ₂ -		O	CH ₂ =CH-CH ₂	188- 190	β

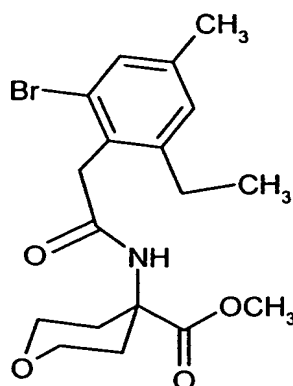
*¹H-NMR (300 MHz, CDCl₃): δ = 2.30 (s, 3H, ArCH₃),
 4.05 (q; 2H, OCH₂-CH₃),
 7.00 (s, 1H, ArH),
 7.30 (s, 1H, ArH) ppm.

5

Example I-d-1

β-isomer

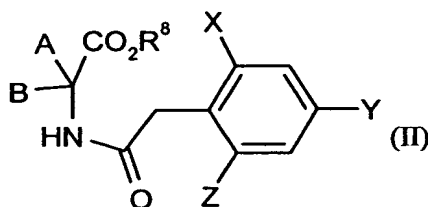
- 0.158 g of the compound of Example I-a-3 is initially charged in 10 ml of dichloromethane, and
 10 0.07 ml of triethylamine is added. 0.03 ml of methanesulphonyl chloride is added a little at a time, and the mixture is stirred at room temperature for 24 h. 5% strength NaHCO₃ solution is added, the organic phase is separated off and the aqueous phase is extracted with dichloromethane. The combined organic phases are dried with sodium sulphate and then, under reduced pressure, evaporated to dryness, and the residue obtained is recrystallized from ethyl acetate/n-heptane 1/1.
- 15 Yield: 0.14 g (70% of theory), m.p. 185-190°C.

Example II-1

Under argon, 4.3 g of methyl 4-aminotetrahydropyranyl-4-carboxylate hydrochloride (0.022 mol) in 50 ml of anhydrous tetrahydrofuran are initially charged in a 100 ml three-necked flask fitted with thermometer and reflux condenser. At 20°C, 6.2 ml (0.044 mol) of triethylamine are added dropwise. The mixture is stirred for another 5 min, and 5.2 g of 2-bromo-6-ethyl-4-methylphenylacetic acid (0.02 mol) are added at 20°C. After 15 min, 4.2 ml of triethylamine (0.03 mol) are added dropwise, followed immediately afterwards by 1.16 ml of phosphorus oxychloride (0.020 mol); the solution should be at moderate boil. The mixture is stirred under reflux for 30 minutes. The solvent is distilled off and the product is purified by silica gel column chromatography (dichloromethane:ethyl acetate, 3:1).

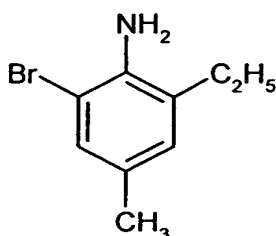
Yield: 7.9 g (92% of theory), m.p. 145°C.

Analogously to Example (II-1) and in accordance with the general statements on the preparation, the following compounds of the formula (II) are obtained



15

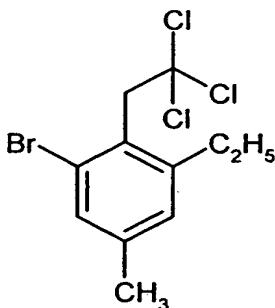
Ex. No.	X	Y	Z	A	B	R ⁸	m.p.°C	isomer
II-2	Br	CH ₃	C ₂ H ₅	-(CH ₂) ₅		CH ₃	120	-
II-3	Br	CH ₃	C ₂ H ₅	-(CH ₂) ₂ -CHOCH ₃ -(CH ₂) ₂ -		CH ₃	146	β
II-4	Br	CH ₃	C ₂ H ₅	-(CH ₂) ₂ -CHOC ₂ H ₅ -(CH ₂) ₂ -		CH ₃	133	β
II-5	Br	CH ₃	C ₂ H ₅	-(CH ₂) ₂ -CHOC ₃ H ₇ -(CH ₂) ₂ -		CH ₃	122	β

Synthesis of 2-bromo-6-ethyl-4-methylphenylacetic acidExample XXI-1

1st step

- 27 g (0.2 mol) of 2-ethyl-4-methylaniline in 300 ml of dichloromethane and 17.8 g (0.22 mol) of sodium acetate (anhydrous) are initially charged at 0 to 5°C. At 0 to 5°C, 2 portions of in each case 16.4 g (0.12 mol) of bromine slowly are added with an interval of 10 minutes, and the mixture is allowed to warm to room temperature. After the reaction has ended (monitored by thin-layer chromatography), 200 g of water and 40 ml of sodium bisulphite are added, the organic phase is separated off and, on a rotary evaporator, concentrated under reduced pressure, and the residue is filtered through silica gel using dichloromethane. The solvent is removed using a rotary evaporator.

Yield: 41.1 g (96% of theory).

Example XX-1

2nd step

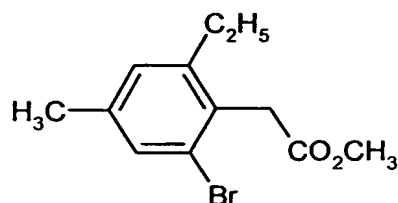
- At room temperature, 41.1 g of 2-bromo-6-ethyl-4-methylaniline (Example XXI-1), 96% pure (0.184 mol), are initially charged in 10 ml of anhydrous acetonitrile. 247 g (2.8 mol) of dichloroethylene are then added dropwise over a period of 5 min, and 29.7 g (0.22 mol) of CuCl₂ (anhydrous) are then added at room temperature. Over a period of 10 min, 29.4 g (0.28 mol) of isobutyronitrile are then added dropwise at room temperature, and the mixture is stirred with cooling. The mixture is then stirred at room temperature for one day.
- After the evolution of gas has ceased, the reaction solution is poured into 750 ml of ice-cold 20% strength HCl and extracted with MTB ether, and the combined organic phases are washed with 20%

strength HCl, dried and, in a fume cupboard and at room temperature, concentrated under reduced pressure using a rotary evaporator.

Yield: 72 g (94% of theory).

The crude product (80% pure) is used without further purification for preparing the ester of the
5 formula XIX-1.

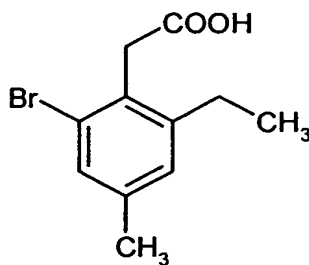
Example XIX-1



3rd step

72 g of the crude product of Example XX-1 are dissolved in 130 ml of methanol, and 117 ml of
30% strength sodium methoxide solution are added dropwise at 0°C. The mixture is then stirred
10 under reflux overnight. After the dropwise addition of 18 ml of concentrated sulphuric acid, the
mixture is again stirred under reflux for 1 h, and the solvent is then removed under reduced
pressure. The residue is taken up in water and extracted with methylene chloride. The organic
phase is dried over magnesium sulphate and concentrated under reduced pressure using a rotary
evaporator. The brown oily residue, with a content of about 75% of the desired product, is used
15 without further purification for preparing the acid XVIII-1.

Example XVIII-1



4th step

At room temperature, 47 g of the compound of Example XIX-1, 75% pure, are initially charged in
275 ml of tetrahydrofuran. At room temperature, 7.3 g of lithium hydroxide, 98% pure (0.173 mol), in
20 280 ml of water are then added dropwise, and the mixture is then stirred at room temperature until the
reaction has ended (monitored by thin-layer chromatography).

The solvent is distilled off under reduced pressure, the residue is extracted with MTB ether and the

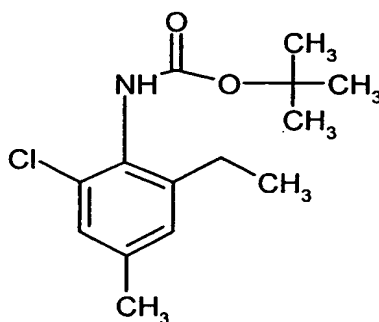
aqueous phase is acidified with 10% strength HCl. The product crystallizes overnight. The precipitate is then filtered off with suction and dried.

Yield: 23.20 g (49% of theory over three steps, starting with Example XXI-1), m.p. 145°C

5 Synthesis of 2-chloro-6-ethyl-4-methylphenylacetic acid

Example A

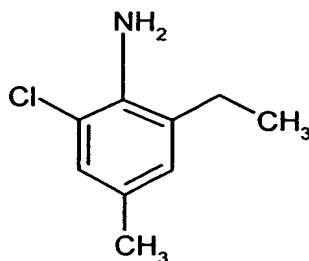
N-(*tert*-Butyloxycarbonyl)-2-chloro-6-ethyl-4-methylaniline



- Under argon and at -40°C, 28 g (115 mmol) of *N*-(*tert*-butyloxycarbonyl)-2-chloro-4-methylaniline are dissolved in 150 ml of dry tetrahydrofuran (THF), and 200 ml of sec-butyllithium (1.4 M solution in hexane, 2.5 eq.) are added slowly. The yellowish mixture is stirred for 2 h and cooled to -78°C, and 15.1 g (138 mmol) of ethyl bromide in 100 ml of THF are added slowly. The mixture is allowed to warm to 25°C overnight, water is added carefully and the mixture is extracted repeatedly with dichloromethane. The combined organic phases are dried over MgSO₄, the solvent is removed under reduced pressure and the crude product is purified by chromatography. This gives 26.6 g (85%) of pure product.

¹H-NMR {400 MHz, DMSO-d₆}: 1.09 (t, ³J_{HH} = 7 Hz, 3H, CH₃); 1.42 (s, 9H, CH₃); 2.27 (s, 3H, CH₃); 2.52 (q, ³J_{HH} = 7 Hz, 2H, CH₂); 7.01 (m, 1H, Ph-H); 7.14 (m, 1H, Ph-H); 8.46 (s, 1H, N-H).

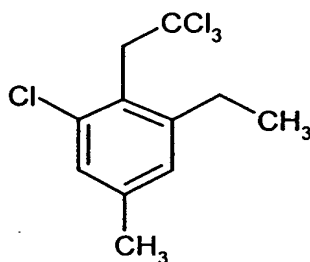
MS/CI: 270 (M+1), 214 (M-tBu).

Example XXI-2*2-Chloro-6-ethyl-4-methylaniline*

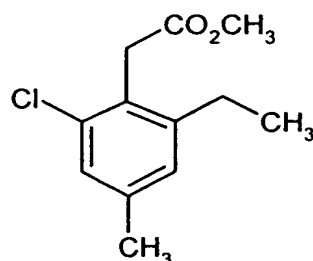
26.6 g (98.6 mmol) of the compound A are dissolved in 150 ml of dichloromethane, trifluoroacetic acid (100 ml) is added and the mixture is stirred at 25°C for 12 h. A further 200 ml of dichloromethane are then added, and the mixture is extracted three times with water. The combined organic phases are dried over MgSO₄ and the solvent is removed under reduced pressure. This gives 12 g (71.7%) of pure product.

¹H-NMR {400 MHz, DMSO-d₆}: 1.12 (t, ³J_{HH} = 7 Hz, 3H, CH₃); 2.13 (s, 3H, CH₃); 2.48 (q, ³J_{HH} = 7 Hz, 2H, CH₂); 4.80 (s, 2H, NH₂); 6.74 (m, 1H, Ph-H); 6.89 (m, 1H, Ph-H).

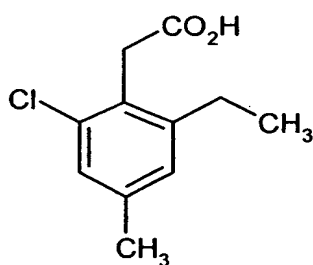
MS/CI: 170 (M+1).

Example XX-2*1'-(2-Chloro-6-ethyl-4-methylphenyl)-2',2',2'-trichloroethane*

10.9 g (106 mmol) of *tert*-butyl nitrite and 11.4 g (85 mmol) of CuCl₂ are suspended in 200 ml of acetonitrile and cooled to 0°C. Over a period of 45 min, 84.4 ml (1.06 mol) of vinylidene chloride are then added dropwise. The reaction mixture is allowed to warm to 25°C, and 12 g (71 mmol) of the compound of Example XXI-2 are then added slowly (30 min). Once the evolution of gas has ceased, the mixture is, with ice-cooling, added to 100 ml of 10% strength HCl. Extraction with methyl *tert*-butyl ether, drying of the organic phases over MgSO₄ and removal of the solvent under reduced pressure gives 21 g of crude product which are immediately reacted further.

Example XIX-2*Methyl- (2-chloro-6-ethyl-4-methylphenyl)acetate*

- 21 g of the compound of Example XX-2 are dissolved in methanol and 45 ml of a 30% strength
 5 methanolic sodium methoxide solution are added slowly at 0°C. The reaction mixture is heated
 under reflux for 12 h, 7 ml of conc. sulphuric acid are added and the mixture is stirred under reflux
 for a further hour. The volatile components are removed under reduced pressure and the residue is
 suspended in water and extracted with dichloromethane. The combined organic phases are dried
 over MgSO₄ and the solvent is removed under reduced pressure. The crude product is obtained as a
 10 dark oil (15.4 g, 60% pure, 57% yield over 2 steps).

Example XVIII-2*2-Chloro-6-ethyl-4-methylphenylacetic acid*

- 15.4 g (60%, 41 mmol) of the compound of Example XIX-2 and 11.4 g (204 mmol) of potassium
 15 hydroxide in 150 ml of methanol/40 ml of water are stirred under reflux for 12 h. The methanol is
 removed under reduced pressure and conc. HCl is then added until the product precipitates out.
 The light-coloured solid is filtered off, washed with water and dried under reduced pressure. This
 gives 7.6 g \triangleq 88% of theory.

- ¹H-NMR {400 MHz, DMSO-d₆}: 1.11 (t, ³J_{HH} = 7 Hz, 3H, CH₃); 2.23 (s, 3H, CH₃); 2.58 (q, ³J_{HH} =
 20 7 Hz, 2H, CH₂); 3.71 (s, 2H, CH₂); 7.01 (m, 1H, Ph-H); 7.13 (m, 1H, Ph-H); 12.5 (s, 1H, CO₂H).

Use examples

Example A

Myzus test (dip treatment)

Solvent: 7 parts by weight of dimethylformamide

5 Emulsifier: 2 parts by weight of alkylaryl polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amounts of solvent and emulsifier, and the concentrate is diluted with emulsifier-containing water to the desired concentration.

10 Cabbage leaves (*Brassica oleracea*), which are heavily infested by the green peach aphid (*Myzus persicae*), are treated by being dipped into the preparation of active compound of the desired concentration.

After the desired period of time, the kill in % is determined. 100% means that all aphids have been killed; 0% means that none of the aphids have been killed.

15 In this test, for example, the following compounds of the Preparation Examples show good activity:

Table A

Plant-damaging insects

Myzus test

5	Active compounds	Concentration of active compound in ppm	Kill rate in % after 6 ^d
	Ex. I-a-1	100	75
	Ex. I-a-4	4	95

Example B

Tetranychus test (OP-resistant/dip treatment)

Solvent: 7 parts by weight of dimethylformamide

Emulsifier: 2 parts by weight of alkylaryl polyglycol ether

- 5 To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amounts of solvent and emulsifier, and the concentrate is diluted with emulsifier-containing water to the desired concentration.

10 Bean plants (*Phaseolus vulgaris*), which are heavily infested by all stages of the greenhouse red spider mite (*Tetranychus urticae*), are dipped into a preparation of active compound of the desired concentration.

After the desired period of time, the activity in % is determined. 100% means that all spider mites have been killed; 0% means that none of the spider mites have been killed.

In this test, for example, the following compounds of the Preparation Examples show good activity:

Table B

Plant-damaging mites

Tetranychus test (OP-resistant/dip treatment)

5	Active compound	Concentration of	Kill rate
		active compound in ppm	in % after 7 ^d
	Ex. I-a-3	4	50

Example C

Aphis gossypii test

Solvent: 7 parts by weight of dimethylformamide

Emulsifier: 2 parts by weight of alkylaryl polyglycol ether

- 5 To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amounts of solvent and emulsifier, and the concentrate is diluted with emulsifier-containing water to the desired concentration.

10 Cotton leaves (*Gossypium hirsutum*), which are heavily infested by the cotton aphid (*Aphis gossypii*), are treated by being dipped into the preparation of active compound of the desired concentration.

After the desired period of time, the kill in % is determined. 100% means that all aphids have been killed; 0% means that none of the aphids have been killed.

In this test, for example, the following compound of the Preparation Examples shows good activity:

Table C

Plant-damaging insects

Aphis gossypii test

5	Active compound	Concentration of	Kill rate
		active compound in ppm	in % after 6 ^d
	Ex. I-a-4	500	80

Example D

Meloidogyne test

Solvent: 7 parts by weight of dimethylformamide

Emulsifier: 2 parts by weight of alkylaryl polyglycol ether

5

To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amounts of solvent and emulsifier, and the concentrate is diluted with water to the desired concentration.

10 Vessels are filled with sand, solution of active compound, *Meloidogyne incognita* egg/larvae suspension and lettuce seeds. The lettuce seeds germinate and the plants develop. On the roots, galls develop.

After the desired period of time, the nematocidal action is determined in % by the formation of galls. 100% means that no galls have been found; 0% means that the number of galls on the treated plants corresponds to that of the untreated control.

15 In this test, for example, the following compound of the Preparation Examples shows good activity:

Table D

Plant-damaging nematodes

Meloidogyne test

5	Active compound	Concentration of	Effect
		active compound in ppm	in % after 14 ^d
	Ex. I-a-1	20	80

Example E**Myzus test (spray treatment)**

5	Solvents:	78	parts by weight of acetone
		1.5	parts by weight of dimethylformamide
	Emulsifier:	0.5	part by weight of alkylaryl polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amounts of solvent and emulsifier, and the concentrate is diluted with emulsifier-containing water to the desired concentration.

- 10 Discs of Chinese cabbage (*Brassica pekinensis*), which are infested by all stages of the green peach aphid (*Myzus persicae*), are sprayed with a preparation of active compound of the desired concentration.

After the desired period of time, the effect in % is determined. 100% means that all aphids have been killed; 0% means that none of the aphids have been killed.

- 15 In this test, for example, the following compounds of the Preparation Examples show good activity:

Table E

Plant-damaging insects

Myzus test (spray treatment)

5	Active compound	Concentration of active compound in g/ha	Kill rate in % after 5 ^d
	Ex. I-a-3	100	100
10	Ex. I-a-1	100	100
	Ex. I-c-3	100	80
	Ex. I-b-5	100	80

Example F

Phaedon larvae test (dip treatment)

Solvent: 7 parts by weight of dimethylformamide

Emulsifier: 2 parts by weight of alkylaryl polyglycol ether

5

To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amounts of solvent and emulsifier, and the concentrate is diluted with emulsifier-containing water to the desired concentration.

10 Cabbage leaves (*Brassica oleracea*) are treated by being dipped into the preparation of active compound of the desired concentration and are populated with larvae of the mustard beetle (*Phaedon cochleariae*) while the leaves are still moist.

After the desired period of time, the kill in % is determined. 100% means that all beetle larvae have been killed; 0% means that none of the beetle larvae have been killed.

15 In this test, for example, the following compound of the Preparation Examples shows good activity:

Table F

Plant-damaging insects

Phaedon larvae test (dip treatment)

5	Active compound	Concentration of	Kill rate
		active compound in ppm	in % after 7 ^d
	Ex. I-a-4	500	100

Example G

Phaedon test (spray treatment)

5	Solvents:	78	parts by weight of acetone
		1.5	parts by weight of dimethylformamide
	Emulsifier:	0.5	parts by weight of alkylaryl polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amounts of solvents and emulsifier, and the concentrate is diluted with emulsifier-containing water to the desired concentration.

- 10 Discs of Chinese cabbage (*Brassica pekinensis*) are sprayed with a preparation of active compound of the desired concentration and, after they have dried, populated with larvae of the mustard beetle (*Phaedon cochleariae*).

After the desired period of time, the activity in % is determined. 100% means that all beetle larvae have been killed; 0% means that none of the beetle larvae have been killed.

- 15 In this test, for example, the following compound of the Preparation Examples shows good activity:

Table G

Plant-damaging insects

Phaedon test

5	Active compound	Concentration of active compound in g/ha	Kill rate in % after 7 ^d
	Ex. I-a-3	100	100

Example H

Tetranychus test (OP-resistant/dip treatment)

Solvent: 7 parts by weight of dimethylformamide

Emulsifier: 2 parts by weight of alkylaryl polyglycol ether

5

To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amounts of solvent and emulsifier, and the concentrate is diluted with emulsifier-containing water to the desired concentration.

10 Bean plants (*Phaseolus vulgaris*), which are heavily infested by all stages of the greenhouse red spider mite (*Tetranychus urticae*), are dipped into a preparation of active compound of the desired concentration.

After the desired period of time, the activity in % is determined. 100% means that all spider mites have been killed; 0% means that none of the spider mites have been killed.

15 In this test, for example, the following compound of the Preparation Examples shows good activity:

Table H

Plant-damaging mites

Tetranychus test (OP-resistant/dip treatment)

5	Active compound	Concentration of active compound in ppm	Kill rate in % after 7 ^d
	Ex. I-a-4	100	99

Example I**Tetranychus test (OP-resistant/spray treatment)**

5	Solvents:	78	parts by weight of acetone
		1.5	parts by weight of dimethylformamide
	Emulsifier:	0.5	part by weight of alkylaryl polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amounts of solvents and emulsifier, and the concentrate is diluted with emulsifier-containing water to the desired concentration.

10 Discs of bean leaves (*Phaseolus vulgaris*) which are infested by all stages of the greenhouse red spider mite (*Tetranychus urticae*) are sprayed with a preparation of active compound of the desired concentration.

After the desired period of time, the activity in % is determined. 100% means that all spider mites have been killed; 0% means that none of the spider mites have been killed.

15 In this test, for example, the following compounds of the Preparation Examples show good activity:

Table I

Plant-damaging mites

Tetranychus test (OP-resistant/spray treatment)

5	Active compound	Concentration of active compound in g/ha	Kill rate in % after 5 ^d
	Ex. I-a-3	100	90
10	Ex. I-c-3	100	80
	Ex. I-b-5	100	70

Example J

Post-emergence test

Solvent: 5 parts by weight of acetone

Emulsifier: 1 part by weight of alkylaryl polyglycol ether

5

To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amount of solvent, the stated amount of emulsifier is added and the concentrate is diluted with water to the desired concentration.

10 Test plants of a height of 5-15 cm are sprayed with the preparation of active compound such that the particular amounts of active compound desired are applied per unit area. The concentration of the spray liquor is chosen such that the particular amounts of active compound desired are applied in 1000 l of water/ha.

After three weeks, the degree of damage in the plants is rated in % damage in comparison to the development of the untreated control.

15 The figures denote:

0% = no effect (like untreated control)

100% = total destruction.

Example K

Pre-emergence test

Solvent: 5 parts by weight of acetone

Emulsifier: 1 part by weight of alkylaryl polyglycol ether

5

To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amount of solvent, the stated amount of emulsifier is added and the concentrate is diluted with water to the desired concentration.

10 Seeds of the test plants are sown in normal soil. After about 24 hours, the soil is sprayed with the preparation of active compound such that the particular amounts of active compound desired are applied per unit area. The concentration of the spray liquor is chosen such that the particular amounts of active compound desired are applied in 1000 l of water/ha.

After three weeks, the degree of damage to the plants is rated in % damage in comparison to the development of the untreated control.

15 The figures denote:

0% = no effect (like untreated control)

100% = total destruction

post-emergence	greenhouse	g of a.i./ha	sugarbeets	Echinochloa	Lolium
Ex. I-a-4		60	0	100	100

pre- emergence	greenhouse	g of a.i./ha	sugarbeets	Echinochloa	Lolium	Setaria
Ex. I-a-4		30	0	80	100	100

Example L**Herbicidal pre-emergence action**

5 Seeds of monocotyledonous and dicotyledonous weed and crop plants are placed into sandy loam in wood fibre pots and covered with soil. The test compounds, formulated in the form of wettable powders (WP), are then, in various dosages as aqueous suspension with a water application rate of 600 l/ha (converted), with 0.2% of wetting agent added, applied to the surface of the covering soil.

10 After the treatment, the pots are placed in a greenhouse and kept under good growth conditions for the test plants. The visual assessment of the emergence damage on the test plants is carried out after a trial period of 3 weeks by comparison with untreated controls (herbicidal effect in per cent (%): 100% effect = the plants have died, 0% effect = like control plants).

Example M**Herbicidal post-emergence action**

15 Seeds of monocotyledonous and dicotyledonous weed and crop plants are placed into sandy loam in wood fibre pots, covered with soil and cultivated in a greenhouse under good growth conditions. 2 - 3 weeks after sowing, the test plants are treated at the one-leaf stage. The test compounds, formulated as wettable powders (WP), are, in various dosages with a water application rate of 600 l/ha (converted), with 0.2% of wetting agent added, sprayed onto the green parts of the plants. After the test plants were kept in the greenhouse under optimum growth conditions for about 20 3 weeks, the effect of the preparations is rated visually in comparison to untreated controls (herbicidal effect in per cent (%): 100% effect = the plants have died, 0% effect = like control plants).

greenhouse post-emergence	g of a.i./ha	Avena sativa	Lolium	Setaria	Sinapis
Ex. I-c-3	320	100	100	100	70
Ex. I-b-5	320	100	100	100	70
Ex. I-c-4	320	100	100	100	80
Ex. I-a-3	320	100	100	100	80

greenhouse post-emergence	g of a.i./ha	Avena sativa	Lolium	Setaria
Ex. I-a-1	320	100	100	80
Ex. I-b-2	320	90	100	100
Ex. I-c-2	320	90	90	80
Ex. I-b-3	320	100	90	100
Ex. I-b-4	320	80	90	90
Ex. I-a-2	320	80	90	100

greenhouse pre-emergence	g of a.i./ha	Avena sativa	Lolium	Setaria	Sinapis	Stellaria
Ex. I-a-1	320	70	80	90	70	100

greenhouse pre-emergence	g of a.i./ha	Lolium	Setaria	Sinapis	Stellaria
Ex. I-b-5	320	100	90	80	-
Ex. I-c-4	320	80	90	70	80

greenhouse pre-emergence	g of a.i./ha	Lolium	Setaria	Amaranthus
Ex. I-a-3	320	80	100	80
Ex. I-c-3	320	100	100	100

Example N

Herbicidal post-emergence action

Seeds of monocotyledonous and dicotyledonous weed and crop plants are placed into sandy loam in wood fibre pots or in plastic pots, covered with soil and cultivated in a greenhouse, during the
5 vegetation period also outdoors outside of the greenhouse, under good growth conditions. 2 - 3 weeks after sowing, the test plants are treated at the one- to three-leaf stage. The test compounds, formulated as wettable powders (WP) or emulsifiable concentrates (EC) are, in various dosages with a water application rate of 300 l/ha (converted), with wetting agent (0.2 to 0.3%) added, sprayed onto the plants and the surface of the soil. 3 - 4 weeks after the treatment of the test plants,
10 the effect of the preparations is rated visually in comparison to untreated controls (herbicidal effect in per cent (%): 100% effect = the plants have died, 0% effect = like control plants).

Use of safeners

If it is additionally to be tested as to whether safeners can improve the plant compatibility of test substances in the case of crop plants, the following options are used for applying the safener:

- 15 - seeds of the crop plants are, before sowing, dressed with the safener substance (the amount of safener is stated in per cent, based on the weight of the seed)
- before the application of the test substances, the crop plants are sprayed with the safener at a certain application rate per hectare (usually 1 day before the application of the test substances)
- the safener is applied together with the test substance as a tank mix (the amount of safener is
20 stated in g/ha or as a ratio, based on the herbicide).

By comparing the effect of the test substances on crop plants without or with safener treatment, it is possible to assess the effect of the safener substance.

Vessel trials with cereals in the greenhouse

Mefenpyr applied 1 day prior to the application of herbicide

	application rate g of a.i./ha	summer barley observed (%)	summer wheat observed (%)
Example I-a-4	50	97	
	25	30	98
	12.5	10	50
Example I-a-4 + mefenpyr	50 + 100	20	
	25 + 100	0	75
	12.5 + 100	0	0

5

	application rate g of a.i./ha	summer barley observed (%)	summer wheat observed (%)
Example I-a-3	100	95	
	50	90	
	25	20	60
Example I-a-3 + mefenpyr	100 + 100	80	
	50 + 100	15	
	25 + 100	0	20

	application rate g of a.i./ha	summer barley observed (%)
Example I-b-5	50	98
	25	65
	12.5	35
Example I-b-5 + mefenpyr	50 + 100	60
	25 + 100	15
	12.5 + 100	10

	application rate g of a.i./ha	summer wheat observed (%)
Example I-b-2	50	98
	25	70
	12.5	20
Example I-b-2 + mefenpyr	50 + 100	70
	25 + 100	30
	12.5 + 100	10

	application rate g of a.i./ha	summer wheat observed (%)
Example I-b-3	50	75
	25	20
	12.5	10
Example I-b-3 + mefenpyr	50 + 100	20
	25 + 100	5
	12.5 + 100	0

	application rate g of a.i./ha	summer barley observed (%)	summer wheat observed (%)
Example I-c-4	25	70	
	12.5	20	60
Example I-c-4 + mefenpyr	25 + 100	20	
	12.5 + 100	5	15

Example O

Critical concentration test / soil insects-treatment of transgenic plants

Test insect: *Diabrotica balteata* - larvae in soil

Solvent: 7 parts by weight of acetone

5 Emulsifier: 1 part by weight of alkylaryl polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amount of solvent, the stated amount of emulsifier is added and the concentrate is diluted with water to the desired concentration.

10 The preparation of active compound is poured onto the soil. Here the concentration of active compound in the preparation is virtually immaterial, only the amount by weight of active compound per unit volume of soil, which is stated in ppm (mg/l), matters. The soil is filled into 0.25 l pots, and they are allowed to stand at 20°C.

15 Immediately after the preparation, 5 pregerminated maize corns of the cultivar YIELD GUARD (trade mark of Monsanto Comp., USA) are placed into each pot. After 2 days, the appropriate test insects are placed into the treated soil. After a further 7 days, the efficacy of the active compound is determined by counting the maize plants that have emerged (1 plant = 20% activity).

Example P

Heliothis virescens test - treatment of transgenic plants

Solvent: 7 parts by weight of acetone

Emulsifier: 1 part by weight of alkylaryl polyglycol ether

- 5 To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amount of solvent and the stated amount of emulsifier, and the concentrate is diluted with water to the desired concentration.

- 10 Soybean shoots (Glycine max) of the cultivar Roundup Ready (trade mark of Monsanto Comp. USA) are treated by being dipped into the preparation of active compound of the desired concentration and are populated with the tobacco bud worm *Heliothis virescens* while the leaves are still moist.

After the desired period of time, the kill of the insects is determined.